

PATENT SPECIFICATION

(11) 1 439 615

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 662 665 668 669 66X 672 675 678 681 694 695 697
 699 761 763 775 790 79Y BD BL BU MB MM QS
 QT QZ TP UF UK UL

(54) SUBSTITUTED ACETATES AND PESTICIDAL COMPOSITIONS CONTAINING THEM

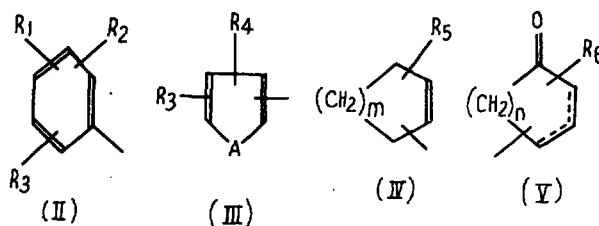
(71) We, SUMITOMO CHEMICAL COMPANY, LIMITED, a Japanese Company, of No. 15, Kitahama 5-Chome, Higashi-Ku, Osaka-Shi, Osaka, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to pesticides, and, more particularly, to substituted acetates which are useful for controlling arthropods; to pesticidal compositions containing as active ingredient at least one such substituted acetate; and to processes for preparing such substituted acetates and pesticidal compositions.

The substituted acetates of this invention are represented by the following general formula (I):



wherein Y represents a group selected from those of the following general formulae (II) to (V):



in which R₁ and R₂ are each independently hydrogen, halogen, cyano, nitro, lower alkyl, lower alkenyl, lower alkynyl, lower alkoxy, lower alkoxyalkyl, halogen-substituted lower alkyl, halogen-substituted lower alkenyl, halogen-substituted lower alkynyl, lower alkylthio, lower alkylsulfoxyl, acyl, acyloxy, lower alkoxy-carbonyl, lower alkenyloxycarbonyl, lower alkynyloxycarbonyl, or R₁ and R₂ together are methylenedioxy, tetramethylene or trimethylene; R₃ and R₄ are each independently hydrogen, halogen, cyano, nitro, lower alkyl, lower alkenyl, lower

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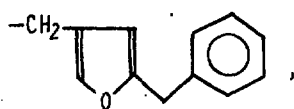
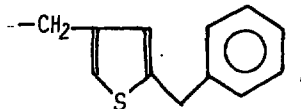
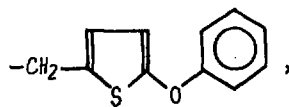
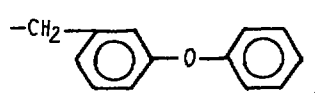
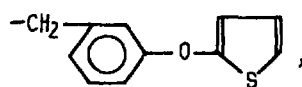
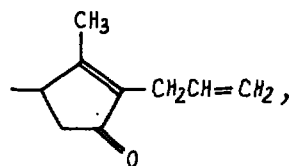
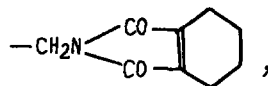
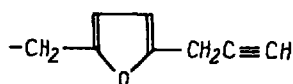


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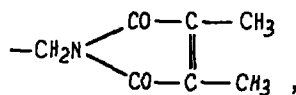
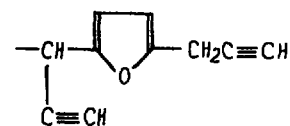
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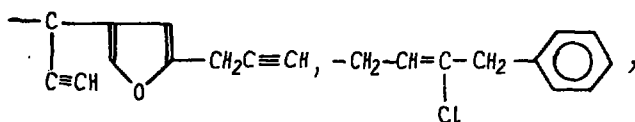
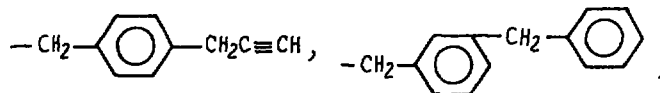
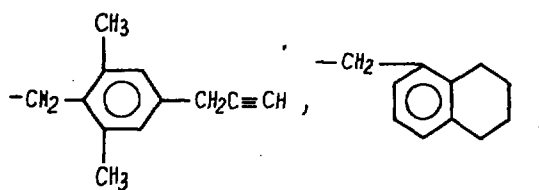
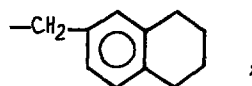
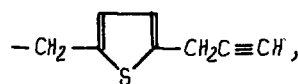
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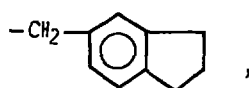
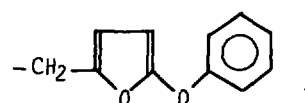
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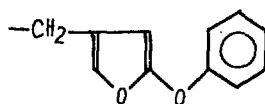
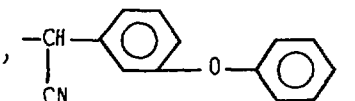
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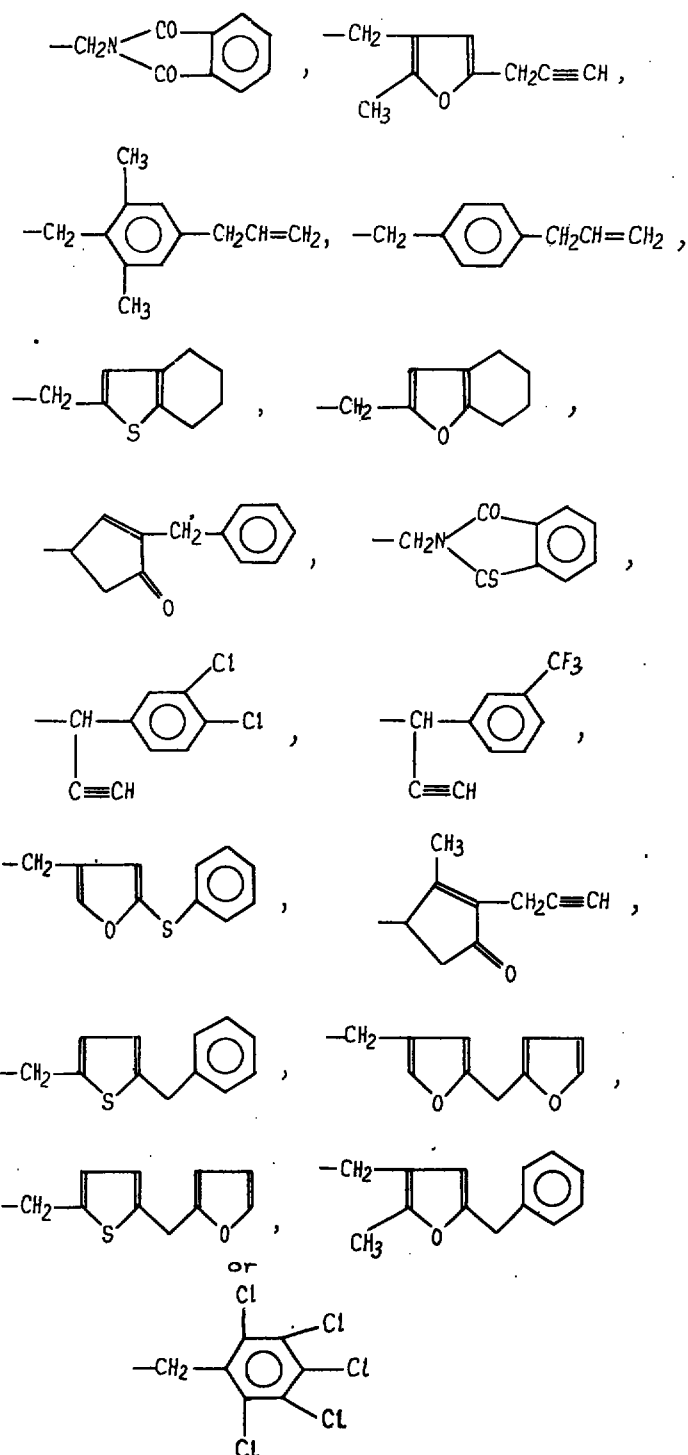


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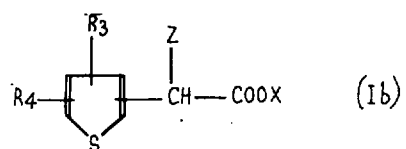
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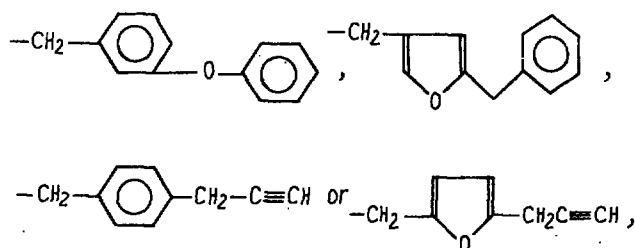
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2) compounds of the formula (Ib)

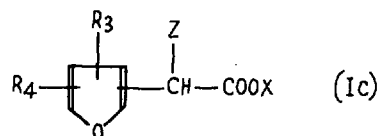
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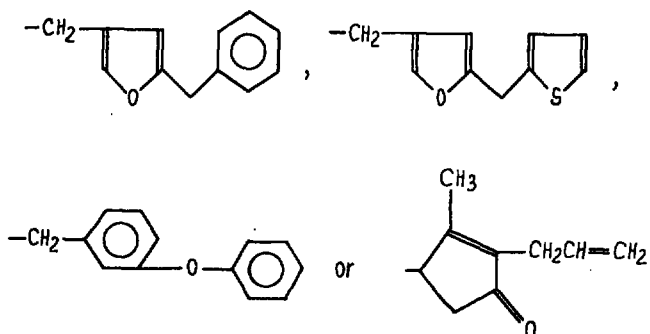
wherein R_3 is hydrogen, methyl, allyl, methoxycarbonyl or acetyl; R_4 is hydrogen; Z is ethyl, propyl or allyl; and X is a group having one of the following formulae:



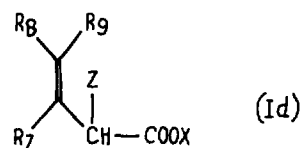
3) compounds of the formula (Ic):



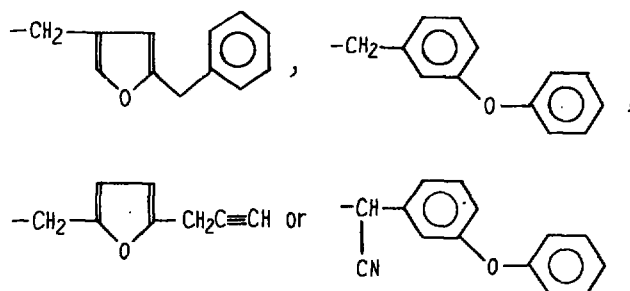
wherein R_3 is hydrogen, methyl, allyl, methoxycarbonyl or butanoyl; R_4 is hydrogen; Z is ethyl or propyl; X is a group having one of the following formulae:



4) compounds of the formula (Id)

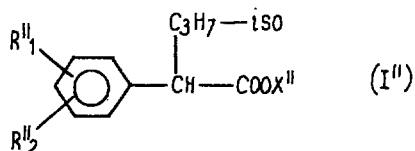


wherein R_7 is hydrogen, methyl or ethyl; R_8 is hydrogen or methyl; R_9 is methyl; Z is C_1-C_3 alkyl; and X is a group having one of the following formulae:

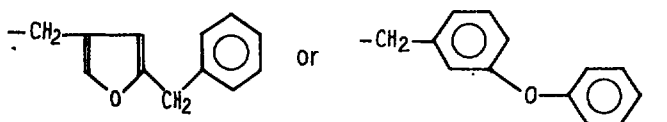


compending application No. 13563/75 (Serial No. 1,439,616). Compounds of the formula (I') have a marked effect on injurious insects, and a low toxicity to mammals. Therefore, the above-mentioned phenylacetic acids are important as intermediates for preparing compounds of the general formula (I).

The substituted acetate compounds of the following general formula (I''):



wherein R''_1 is straight or branched chain C_1-C_4 alkyl, C_1-C_4 alkoxy or halogen; R''_2 is hydrogen or, together with R''_1 , methylenedioxy; and X'' is a group of the formula



are better in insecticidal effect and knock-down effect than most other substituted acetate compounds of the formula (I). Preferred acetates of formula (I'') are those in which R''_2 is hydrogen and R''_1 is a *p*-substituent selected from halogen, methoxy or lower alkyl.

Since BHC and DDT were developed, remarkable advances have been made in the field of organic agricultural pesticides such as organic phosphorus compounds, carbamates, pyrethroids and progress in the development of such organic agricultural agents has led to the establishment of a close correlation between the quantity of pesticide applied and the quantity of crops harvested. On the other hand, however, the use of these agricultural pesticides has caused environmental pollution, giving rise to such problems as the accumulation of toxicity and chronic toxicity, as well as generating a wide variety of pesticide-resistant noxious insects. The requirements desired of a pesticide are, therefore, that besides exhibiting activity it should also exhibit a low undesirable toxicity, low residual characteristics, rapid decomposition and be converted into a non-toxic material on entry into one of the biological cycles of the ecological system. In particular, compounds containing no heavy metals or halogen atoms and composed mainly of carbon, hydrogen and oxygen are considered to be advantageous as agricultural pesticides.

The active constituents of the pesticides presently used include organic phosphorus compounds, carbamates, chrysanthemic acid esters and organo-chlorine compounds, and most researchers in this field now endeavour to develop new types of pesticides by considering the efficiency of each of the above constituents and screening various synthetic derivatives, retaining only those which are superior to the known pesticides.

We consider that each of the above well-known active constituents has certain inherent basic pesticidal characteristics specific to its active group and that the disadvantages associated with the specific active group would not be eliminated without also losing the basic pesticidal characteristics. As a result of extensive researches for active constituents having novel chemical structures, we have found the new and useful acetic acid esters represented by the above formula (I).

The compounds of the formula (I) have various broad advantages and also exhibit strong selectivity, and only the chemical structures retaining properties advantageous for agricultural agents are comprehended by compounds of the general formula (I).

Heretofore, ester groups which are considered to be pesticidally active, for example, phosphoric acid esters and chrysanthemic acid esters were believed to derive their activity from the basic structure of phosphoric acid and cyclopropanecarboxylic acid, respectively. The phosphoric acid esters contain a sulfur, or an oxygen, atom bonded to a pentavalent phosphorus atom by a double bond as an essential structural feature and the chrysanthemic acid esters have a three-membered ring as an essential structural feature; and their pesticidal activity tends

to be strengthened or weakened depending upon the type of moieties present in the vicinity of nucleus represented by the above essential structure.

In the compounds of the formula (I), the acid moiety represented by the following general formula (XI):



is considered to be an important part of the basic active structure, and the essential structure is completed by a hydrogen atom at the α -position of the acid moiety; an appropriate substituent Z and a substituent Y which are characterized by their planar structure. The alcohol moiety of the ester corresponds to the alcohol moiety of the well-known chrysanthemic acid esters as shown by the examples of compounds described below, but, in accordance with the present invention, it was found that highly active pesticides could be prepared by esterification of the acids represented by the formula (XI) with the above alcohol moiety and that compounds having a surprisingly high selectivity could be prepared by using an appropriate combination of an acid moiety and an alcohol moiety. However, the order of activity of an ester composed of a known alcohol and a known acid cannot be directly applied to the evaluation of the activity of an ester of the formula (I), since these esters exhibit activities entirely different from those of the known esters. Accordingly, an ester composed of an acid moiety comprehended by general formula (I) and an alcohol which has been found to form a known ester of high pesticidal activity does not necessarily exhibit excellent activity.

In addition, in accordance with the present invention, various advantages such as immediate onset of action, permeability, transfer into living plants, residual activity, pesticidal activity, metamorphosis disturbance, sterilization, and inhibition of egg-laying can freely be controlled by appropriately selecting a combination of an acid and one of a wide variety of alcohols. Also, with respect to the spectrum of pesticidal activity, the compounds of the formula (I) exhibit a selective or non-selective activity on such orders as *Coreoptera*, *Lepidoptera*, *Diptera*, *Orthoptera*, *Hemiptera*, *Homoptera* and *Acarus*, depending upon the specific combination of acid and an alcohol. Furthermore, the compounds of the formula (I) are useful for controlling noxious insects such as *Nematoda*; other of their important features are that they are active against noxious insects which are resistant to the pesticides presently used, because their basic structures differ from those of the known pesticides to which the insects are resistant; and that they have very low toxicity to mammals including man as indicated by the results of the Experiments given below.

In preparing the substituted acetic acid esters represented by the formula (I), an acid represented by the general formula (XI) or a reactive derivative thereof is reacted with an alcohol represented by the following general formula (XII):



wherein X is as defined above, or a halide or sulfoxylate thereof.

The term "reactive derivative" of the acid is used herein to mean an acid halide, an acid anhydride, an ester with an alcohol having a low boiling point, an alkali metal salt, a silver salt or an organic tertiary base salt of the acid.

The substituted acetic acid esters represented by the formula (I) include optical isomers due to the carbon atom at α -position, and it is to be understood that compounds of the formula (I) include such optical isomers.

In carrying out the production of the substituted acetic acid esters of the formula (I), the esterification between the acid (XI) and the alcohol (XII) can advantageously be accomplished by reacting the reactants in an appropriate inert solvent at room temperature or at an elevated temperature under appropriate dehydrating conditions, e.g., in the presence of cyclohexylcarbodiimide. When an acid halide is used as a reactive derivative of the acid (XI), the desired ester can be obtained in high yield by reacting the alcohol (XII) and the acid halide at room temperature using an acid acceptor, for example, an organic tertiary amine such as pyridine, or triethylamine. The acid halides which may be used to prepare a compound of the formula (I) may be any type of corresponding halide, but an acid chloride is generally preferred. The presence of an inert solvent is not essential to the esterification reaction, but it is generally preferred to use a solvent in order to

assure a smooth reaction. Any solvent which is inert to the reactants and the ester product may be used and a preferred inert solvent includes benzene, toluene and petroleum benzene. When an ester of the acid (XI) and a low boiling point alcohol, e.g., methanol or, ethanol are used as the reactants, the desired ester (I) may be obtained in high yield by reacting the ester and the alcohol (XII) with heating in the presence of an appropriate organic base catalyst, preferably, an alkali metal alkoxide corresponding to the low boiling alcohol of the ester used or sodium hydride in an inert solvent, such as toluene, while removing a low boiling alcohol liberated during the reaction from the reaction system by a fractional distillation column.

In an alternative esterification procedure using an acid anhydride as a reactive derivative of the acid (XI), the desired ester can be obtained by reacting the acid anhydride with the alcohol (XII) at room temperature without using specific reaction aids. In this case, it is preferred to heat the reaction system and to use a solvent such as toluene or, xylene in order to ensure a smooth reaction, but the heating and the use of solvent are not critical in this procedure.

When a halide or sulfoxylate of the above alcohol (XII) is used, the acid (XI) is generally employed in the form of an alkali metal salt, a silver salt or an organic tertiary base salt. These salts may be formed *in situ* by adding simultaneously the acid (XII) and the corresponding base to the reaction system. In this case, a solvent such as benzene, acetone or dimethylformamide is preferably used, and the reaction is preferably conducted by heating the reaction system at or below the boiling point of the solvent used. Preferred halides of the alcohol (XII) are the chlorides and bromide.

Representative examples of the compounds of the formula (I) are shown in the accompanying drawings as compounds Nos. 1 to 128, each compound being identified by its structural formula and specific name.

The process for preparing the esters of the general formula (I) will now be illustrated by the following Preparations Nos. 1 to 229 set forth in the following Preparative Table: Preparations Nos. 1 to 57 relate to the preparation of selected ones of Compounds Nos. 1 to 128 shown in the drawing, while the subsequent Preparations relate to the preparation of further Compounds Nos. 129 to 300 of the general formula (I).

In the Table, the symbols "a", "b", "c", "d", and "e" stand for the following esterification methods.

a: Esterification using an acid chloride.

b: Esterification using an acid anhydride.

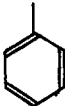
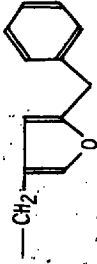
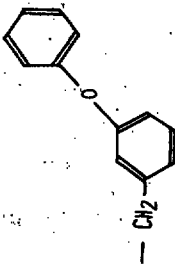
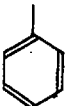
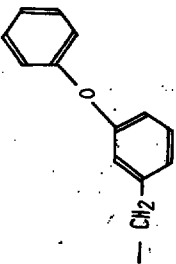
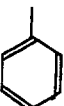
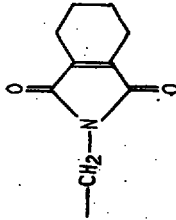
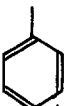
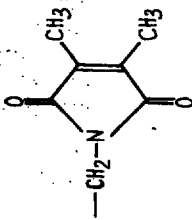
c: Dehydration esterification of an acid and an alcohol with dicyclohexylcarbodiimide in an inert solvent.

d: Esterification by transesterification using sodium hydride as a catalyst in toluene.

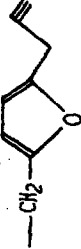
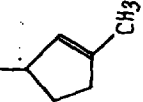
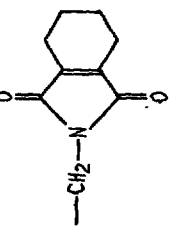
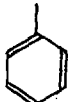
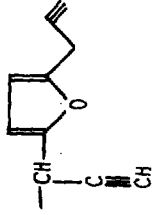
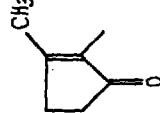
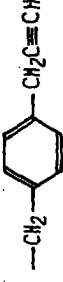
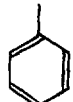
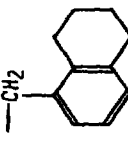
e: Esterification using a silver or a triethylammonium salt of acid and a halide of an alcohol.

Preparations Nos. 1, 2, 5, 17, 22, 27, 46 and 48 are later described in detail and illustrate the above five methods.

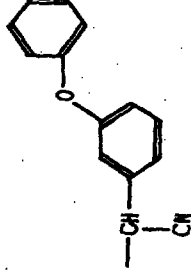
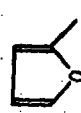
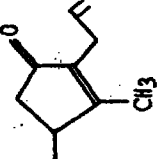
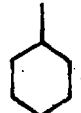
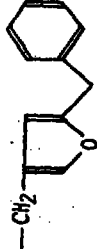
PREPARATIVE TABLE

Preparation Exp. No.	Comp. No.	Z	Y	X	Esteri- fication Method	Yield (%)	Physical Formula Calcd. (%)	Properties Refractive Index Found (%)
1	1	CH ₃ CH ₂ —			b	85	C ₂₂ H ₂₂ O ₃ C: 79.01 H: 6.63	n _D ¹⁷ 1.5545 78.91 6.54
2	2	CH ₃ CH ₂ —			a	91	C ₂₃ H ₂₂ O ₃ C: 79.74 H: 6.40	n _D ²² 1.5712 79.65 6.41
3	3	CH ₃ CH ₂ O—			e	80	C ₂₃ H ₂₂ O ₄ C: 76.22 H: 6.12	n _D ²⁴ 1.5275 76.19 6.17
4	4	CH ₃ CH ₂ —			a	92	C ₁₉ H ₁₇ O ₄ N C: 70.57 H: 5.30 N: 4.33	n _D ²² 1.5403 70.61 5.28 4.25
5	5	CH ₂ =CH—CH ₂ —			e	75	C ₁₈ H ₁₉ O ₄ N C: 68.99 H: 6.11 N: 4.47	n _D ²² 1.5349 67.01 6.09 4.42

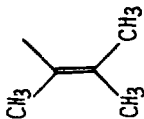
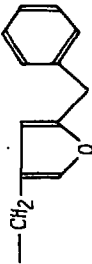
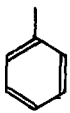
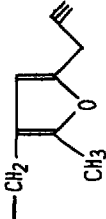
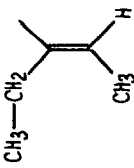
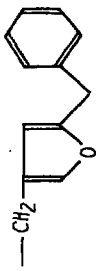
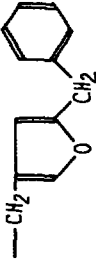
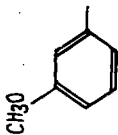
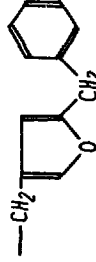
PREPARATIVE TABLE

Preparation Exp. No.	Comp. No.	Z	Y	X	Esteri- fication Method	Yield (%)	Physical Formula Calcd. (%)	Properties Refractive Index Found (%)
6	6	CH_3CH_2-			a	81	$\text{C}_{10}\text{H}_{16}\text{O}_2\text{S}$ C: 66.64 H: 5.59 S: 11.12	n_D^{25} 1.5835 66.59 5.50 11.18
7	7	CH_3-			e	85	$\text{C}_{10}\text{H}_{13}\text{O}_4\text{N}$ C: 68.12 H: 7.31 N: 4.41	n_D^{25} 1.5648 68.09 7.22 4.50
8	8	CH_3CH_2-			a	83	$\text{C}_{20}\text{H}_{18}\text{O}_3$ C: 78.41 H: 5.92	$n_D^{24.5}$ 1.5310 78.3 5.86
9	9	CH_3CH_2-			a	84	$\text{C}_{22}\text{H}_{24}\text{O}_4$ C: 74.97 H: 6.86	n_D^{22} 1.5123 75.06 6.80
10	10	CH_3CH_2-			a	90	$\text{C}_{20}\text{H}_{20}\text{O}_2$ C: 82.15 H: 6.89	n_D^{23} 1.5039 82.05 6.93
11	11	CH_3-			a	93	$\text{C}_{20}\text{H}_{22}\text{O}_2$ C: 81.60 H: 7.53	n_D^{24} 1.5536 81.52 7.58

PREPARATIVE TABLE

Preparation Exp. No.	Comp. No.	Z	Y	X	Esteri- fication Method (%)	Yield (%)	Physical Formula Calcd. (%)	Properties Refractive Index Found (%)
12	12	CH ₃ CH ₂ —			a	91	C ₁₂ H ₁₄ O ₂ S C: 75.39 H: 6.32 S: 9.15	n _D ²² 1.5488 75.29 6.27 9.20
13	13	CH ₃ >CH— CH ₃			a	90	C ₁₂ H ₁₄ O ₂ S C: 75.78 H: 6.64 S: 8.79	n _D ²² 1.5613 75.70 6.69 8.81
14	14	CH ₃ CH ₂ —			a	71	C ₁₂ H ₁₃ O ₂ N C: 77.60 H: 5.70 N: 3.77	n _D ²² 1.5638 77.49 5.97 3.79
15	15	BrCH ₂ CH ₂ —			a	89	C ₁₂ H ₁₃ O ₂ Br C: 64.08 H: 5.13 Br: 19.38	n _D ²² 1.5911 64.11 5.11 19.29
16	16	CH ₃ CH ₂ —			a	90	C ₁₂ H ₁₄ O ₂ C: 70.81 H: 6.99	n _D ²² 1.5118 70.89 6.77
17	17				d	72	C ₁₆ H ₁₈ O ₂ C: 80.38 H: 7.27	mp 51~53°C 80.41 7.24

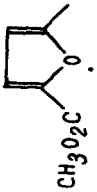
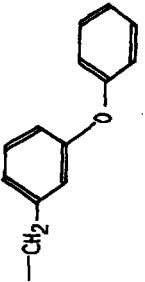
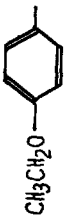
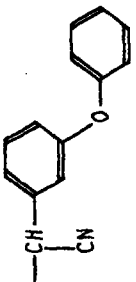
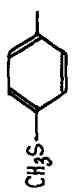
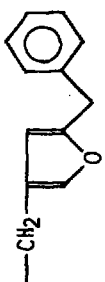
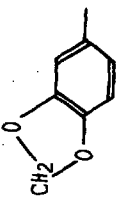
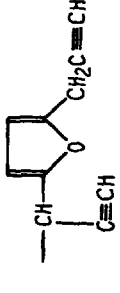
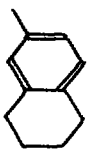
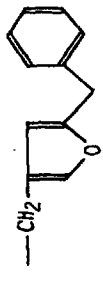
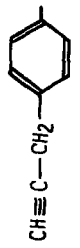
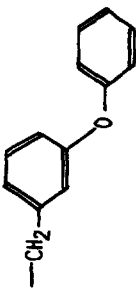
PREPARATIVE TABLE

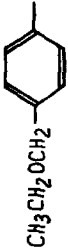
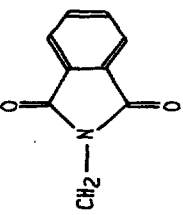
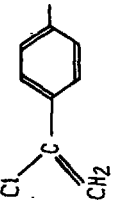
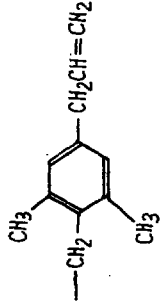
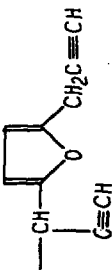
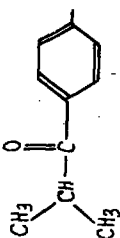
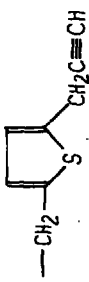
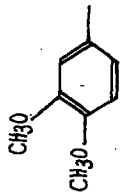
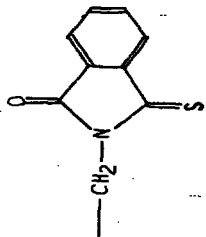
Preparation Exp. No.	Comp. No.	Z	Y	X	Esteri- fication Method	Yield (%)	Physical Formula Calcd. (%)	Properties Refractive Index Found (%)
18	18	CH_3CH_2-			a	84	$\text{C}_{21}\text{H}_{26}\text{O}_3$ C: 77.27 H: 8.03	n_D^{23} 1.5417 77.41 7.96
19	19	$\text{CH}_2-\text{CH}=\text{CH}_2$			a	80	$\text{C}_{21}\text{H}_{22}\text{O}_3$ C: 78.23 H: 6.88	n_D^{24} 1.5632 78.19 6.94
20	20	$\text{CH}_2=\text{CH}-\text{CH}_2-$			a	90	$\text{C}_{17}\text{H}_{16}\text{O}_3\text{S}$ C: 67.98 H: 5.37 S: 10.68	n_D^{22} 1.5274 68.07 5.36 10.64
21	21	CH_3-			a	88	$\text{C}_{20}\text{H}_{24}\text{O}_3$ C: 76.89 H: 7.74	n_D^{21} 1.5693 76.80 7.71
22	22	$\text{CH}_3-\text{CH}=\text{CH}_3$			a	88	$\text{C}_{24}\text{H}_{26}\text{O}_4$ C: 76.16 H: 6.93	n_D^{17} 1.5470 76.20 6.89
23	23	CH_3CH_2-			b	83.2	$\text{C}_{23}\text{H}_{24}\text{O}_4$ C: 75.80 H: 6.64	n_D^{25} 1.5481 75.71 6.69

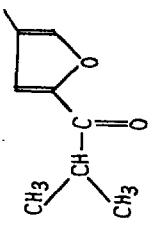
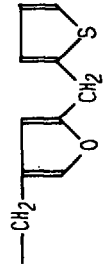
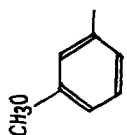
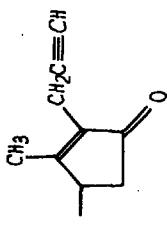
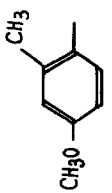
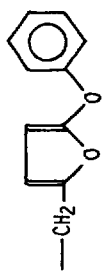
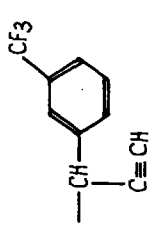
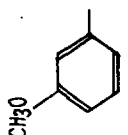
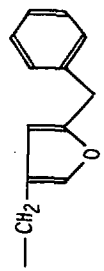
PREPARATIVE TABLE

Preparation Exp. No.	Comp. No.	Z	Y	X	Esteri- fication Method	Yield (%)	Physical Formula Calcd. (%)	Properties Refractive Index Found (%)
24	24	$\text{CH}_3 > \text{CH}-\text{CH}_3$			e	79.8	$\text{C}_{16}\text{H}_{18}\text{O}_3$ C: 74.26 H: 6.71	n_D^{25} 1.5655 74.25 6.77
25	25	CH_3CH_2-			e	81.5	$\text{C}_{15}\text{H}_{16}\text{O}_3$ C: 74.24 H: 5.98	n_D^{25} 1.5621 74.11 6.09
26	26	CH_3CH_2-			a	90.1	$\text{C}_{15}\text{H}_{16}\text{O}_3$ C: 69.67 H: 6.10 S: 8.09	n_D^{25} 1.5448 69.55 6.11 8.11
27	27	CH_3CH_2-			c	61.2	$\text{C}_{22}\text{H}_{21}\text{O}_4\text{N}$ C: 71.52 H: 7.37 N: 3.79	n_D^{25} 1.5399 71.60 7.29 3.85
28	28	$\text{CH}_3 > \text{CH}-\text{CH}_3$			a	92.2	$\text{C}_{15}\text{H}_{16}\text{O}_3$ C: 66.66 H: 5.59 F: 15.06	n_D^{25} 1.5368 66.61 5.62 15.11
29	30	$\text{CH}_2=\text{CH}-\text{CH}_2-$			a	82.5	$\text{C}_{22}\text{H}_{24}\text{O}_4$ C: 74.97 H: 6.86	n_D^{25} 1.5566 75.02 6.04

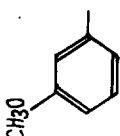
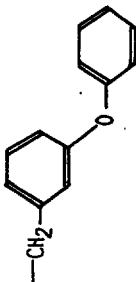
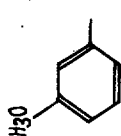
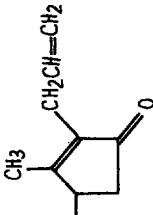
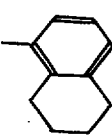
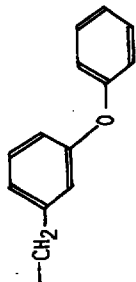
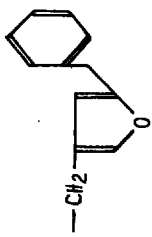
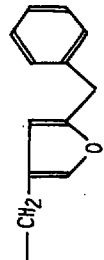
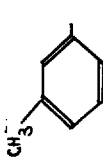
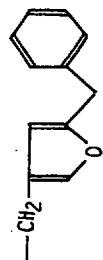
PREPARATIVE TABLE

Preparation		Z	Y	X	Esterification Method	Yield (%)	Physical Formula Calcd. (%)	Properties	
Exp. No.	Comp. No.							Refractive Index	Found (%)
30	33	$\text{CH}_3 > \text{CH} -$ CH_3			e	81.8	$\text{C}_{24}\text{H}_{24}\text{O}_6$ C: 70.57 H: 5.92	n_D^{25} 1.5367 70.56 5.89	
31	34	$\text{CH}_3 > \text{CH} -$ CH_3			a	92.5	$\text{C}_{27}\text{H}_{27}\text{O}_4\text{N}$ C: 75.50 H: 6.34 N: 3.26	n_D^{25} 1.5208 75.19 6.30 3.31	
32	35	$\text{CH}_3 > \text{CH} -$ CH_3			a	95.3	$\text{C}_{24}\text{H}_{26}\text{O}_3\text{S}$ C: 73.06 H: 6.64 S: 8.13	n_D^{25} 1.5335 73.10 6.64 8.15	
33	37	$\text{CH}_3 > \text{CH} -$ CH_3			a	73.6	$\text{C}_{22}\text{H}_{20}\text{O}_3$ C: 72.51 H: 5.53	n_D^{25} 1.5236 72.55 5.61	
34	36	$\text{CH}_3 > \text{CH} -$ CH_3			d	86.2	$\text{C}_{27}\text{H}_{30}\text{O}_3$ C: 80.56 H: 7.51	80.61 7.46	
35	45	$\text{CH}_3\text{CH}_2 -$			e	78.1	$\text{C}_{26}\text{H}_{24}\text{O}_3$ C: 81.22 H: 6.29	81.20 6.31	

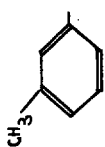
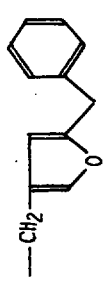
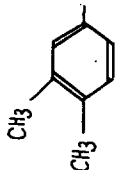
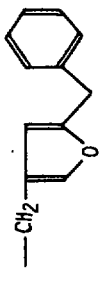
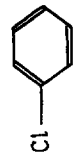
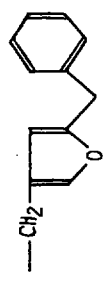
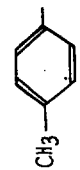
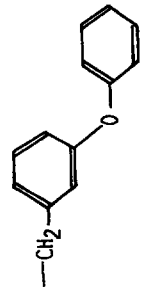
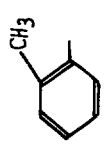
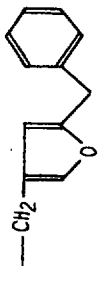
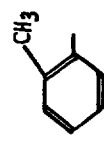
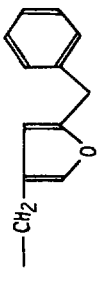
Preparation Exp. No.	Comp. No.	Z	Y	X	Esteri- fication Method	Yield (%)	Physical Formula Calcd. (%)	Properties Refractive Index Found (%)
36	48	$\text{CH}_3 > \text{CH}-$ CH_3			a	92.7	$\text{C}_{21}\text{H}_{23}\text{O}_5\text{N}$ C: 69.85 H: 6.37 N: 3.54	$n_D^{25} 1.5221$ 69.78 6.39 3.55
37	49	$\text{CH}_3 > \text{CH}-$ CH_3			a	91.2	$\text{C}_{21}\text{H}_{23}\text{O}_5\text{Cl}$ C: 75.64 H: 7.36 Cl: 8.93	$n_D^{25} 1.5413$ 75.66 7.39 8.87
38	51	$\text{CH}_3 > \text{CH}-$ CH_3			a	84.6	$\text{C}_{22}\text{H}_{22}\text{O}_4$ C: 75.41 H: 6.33	$n_D^{25} 1.5253$ 75.40 6.22
39	52	CH_3CH_2-			a	81.2	$\text{C}_{22}\text{H}_{24}\text{O}_3\text{S}$ C: 71.71 H: 6.56 S: 8.70	$n_D^{25} 1.5549$ 71.80 6.59 8.78
40	55	$\text{CH}_2=\text{CH}-\text{CH}_2-$			a	86.9	$\text{C}_{22}\text{H}_{21}\text{O}_3\text{NS}$ C: 64.21 H: 5.15 N: 3.40 S: 7.79	$n_D^{19} 1.5350$ 64.30 5.19 3.29 7.72

Preparation Exp. No.	Comp. No.	Z	Y	X	Esteri- fication Method	Yield (%)	Physical Formula Calcd. (%)	Properties Refractive Index Found (%)
41	56	$\text{CH}_3 > \text{CH} -$ CH_3			c	72.1	$\text{C}_{23}\text{H}_{26}\text{O}_5\text{S}$ C: 66.64 H: 6.32 S: 7.14	$n_D^{22} 1.5324$ 66.57 6.40 7.71
42	67	$\text{CH}_3 > \text{CH} -$ CH_3			a	93.7	$\text{C}_{21}\text{H}_{24}\text{O}_4$ C: 74.09 H: 7.11	$n_D^{25} 1.5628$ 74.06 7.22
43	61	$\text{CH}_3 > \text{CH} -$ CH_3			a	93.2	$\text{C}_{24}\text{H}_{26}\text{O}_5$ C: 73.07 H: 6.64	$n_D^{25} 1.5501$ 73.11 6.57
44	69	$\text{CH}_3\text{CH}_2 -$			b	78.9	$\text{C}_{21}\text{H}_{19}\text{O}_3\text{F}_3$ C: 67.01 H: 5.09 F: 15.15	$n_D^{25} 1.5119$ 66.95 5.14 15.20
45	81	$\text{CH}_3 > \text{CH} -$ CH_3			d	84.8	$\text{C}_{24}\text{H}_{26}\text{O}_4$ C: 76.16 H: 6.93	$n_D^{16} 1.5411$ 76.22 6.94

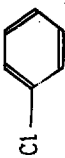
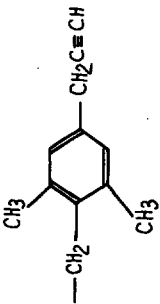
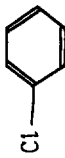
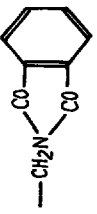
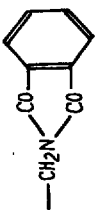
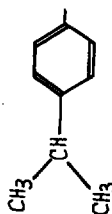
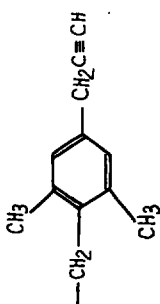
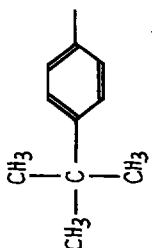
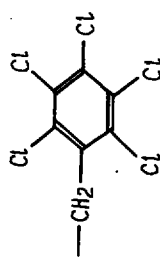
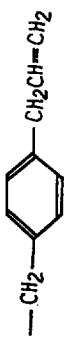
PREPARATIVE TABLE

Preparation Exp. No.	Comp. No.	Z	Y	X	Esteri- fication Method (%)	Physical Formula Calcd. (%)	Properties Refractive Index Found (%)
46	87	$\text{CH}_3 > \text{CH} -$ CH_3			d	$\text{C}_{25}\text{H}_{26}\text{O}_4$ C: 76.90 H: 6.71	n_D^{17} 1.5377 76.85 6.76
47	93	$\text{CH}_3\text{CH}_2 -$			b	$\text{C}_{20}\text{H}_{24}\text{O}_4$ C: 73.14 H: 7.37	n_D^{19} 1.5211 73.19 7.30
48	43	$\text{CH}_3 > \text{CH} -$ CH_3			e	$\text{C}_{28}\text{H}_{30}\text{O}_3$ C: 81.12 H: 7.30	n_D^{20} 1.5660 81.20 7.27
49	102	$\text{CH}_3\text{CH}_2 -$			a	$\text{C}_{23}\text{H}_{24}\text{O}_3$ C: 79.28 H: 6.94	n_D^{25} 1.5474 79.32 7.10
50	103	$\text{CH}_3 > \text{CH} -$ CH_3			a	$\text{C}_{24}\text{H}_{26}\text{O}_3$ C: 79.53 H: 7.23	n_D^{25} 1.5433 79.60 7.18
51	104	$\text{CH}_3\text{CH}_2 -$			a	$\text{C}_{23}\text{H}_{24}\text{O}_3$ C: 79.28 H: 6.94	n_D^{25} 1.5470 79.23 6.99 (

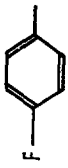
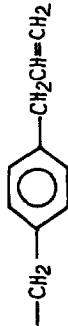
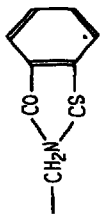
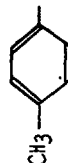
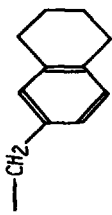
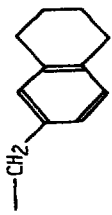
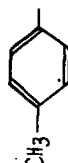
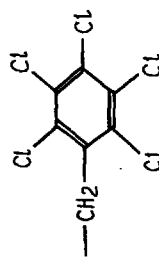
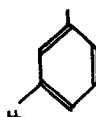
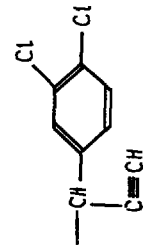
PREPARATIVE TABLE

Preparation Exp. No.	Comp. No.	Z	Y	X	Esteri- fication Method (%)	Physical Formula Calcd. (%)	Properties Refractive Index Found (%)
52	105	$\text{CH}_3 > \text{CH} -$ CH_3			a	$\text{C}_{24}\text{H}_{26}\text{O}_3$ C: 79.53 H: 7.23	$n_D^{25.5}$ 1.5430 79.50 7.30
53	106	$\text{CH}_3 > \text{CH} -$ CH_3			a	$\text{C}_{25}\text{H}_{28}\text{O}_3$ C: 79.75 H: 7.50	$n_D^{25.5}$ 1.5238 79.79 7.49
54	107	$\text{CH}_3 > \text{CH} -$ CH_3			a	$\text{C}_{23}\text{H}_{23}\text{O}_3\text{Cl}$ C: 72.15 H: 6.05 Cl: 9.26	$n_D^{25.5}$ 1.5241 72.18 6.10 9.29
55	108	$\text{CH}_3 > \text{CH} -$ CH_3			a	$\text{C}_{25}\text{H}_{26}\text{O}_3$ C: 80.18 H: 7.00	$n_D^{28.5}$ 1.5596 80.21 6.92
56	109	$\text{CH}_3 - \text{CH} -$ CH_3			a	$\text{C}_{24}\text{H}_{26}\text{O}_3$ C: 77.53 H: 7.23	$n_D^{26.5}$ 1.5431 79.60 7.21
57	110	$\text{CH}_3\text{CH}_2 -$			a	$\text{C}_{23}\text{H}_{24}\text{O}_3$ C: 79.28 H: 6.94	$n_D^{26.5}$ 1.5501 79.40 7.11

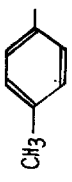
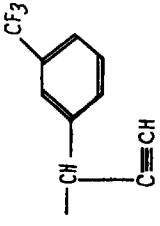
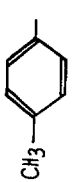
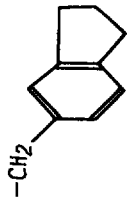
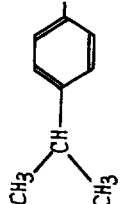
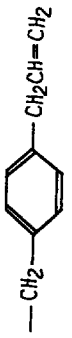
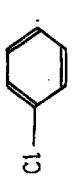
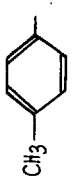
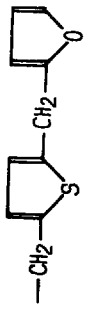
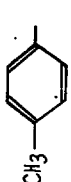
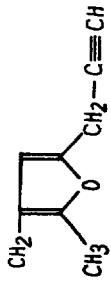
PREPARATIVE TABLE

Preparation Exp. No.	Comp. No.	Z	Y	X	Esteri- fication Method (%)	Physical Formula Calcd. (%)	Properties Refractive Index Found (%)
58	129	$\text{CH}_3 > \text{CH} -$ CH_3			b	$\text{C}_{12}\text{H}_{10}\text{O}_2\text{Cl}$ C: 74.88 H: 6.83 Cl: 9.61	n_D^{20} 1.5423 74.79 6.81 9.63
59	130	$\text{CH}_3 > \text{CH} -$ CH_3			c	$\text{C}_{20}\text{H}_{18}\text{O}_4\text{NCl}$ C: 64.60 H: 4.88 N: 3.77 Cl: 9.54	n_D^{20} 1.5501 64.63 4.86 3.79 9.53
60	131	$\text{CH}_3 > \text{CH} -$ CH_3			e	$\text{C}_{20}\text{H}_{18}\text{O}_4\text{NBr}$ C: 57.70 H: 4.36 N: 3.37 Br: 19.20	n_D^{20} 1.5383 57.80 4.39 3.37 19.28
61	132	$\text{CH}_3 > \text{CH} -$ CH_3			a	$\text{C}_{26}\text{H}_{22}\text{O}_2$ C: 82.93 H: 8.57	n_D^{20} 1.5433 82.88 8.63
62	133	$\text{CH}_3 > \text{CH} -$ CH_3			a	$\text{C}_{22}\text{H}_{20}\text{O}_2\text{Cl}_3$ C: 53.20 H: 4.67 Cl: 35.69	n_D^{20} 1.5211 53.38 4.68 35.71
63	134	$\text{CH}_3 > \text{C} -$ $\text{CH}_3 \quad \text{CH}_3$			a	$\text{C}_{23}\text{H}_{20}\text{O}_2$ C: 82.10 H: 8.39	82.19 8.41

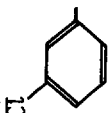
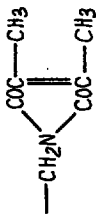
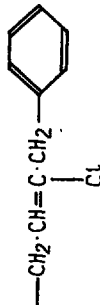
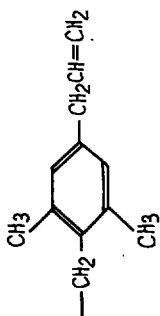
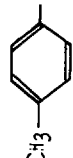
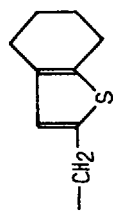
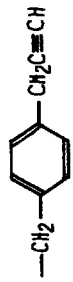
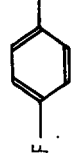
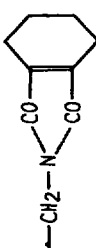
PREPARATIVE TABLE

Preparation Exp. No.	Comp. No.	Z	Y	X	Esteri- fication Yield Method (%)	Physical Formula Calcd. (%)	Properties Refractive Index Found (%)
64	135	$\text{CH}_3 > \text{CH} -$ CH_3			a	$\text{C}_{21}\text{H}_{23}\text{O}_2\text{F}$ C: 77.27 H: 7.10 F: 5.82	77.32 7.03 5.91
65	136	$\text{CH}_3 > \text{CH} -$ CH_3			a	$\text{C}_{21}\text{H}_{23}\text{O}_2\text{NS}$ C: 68.64 H: 5.76 N: 3.81 S: 8.73	n_D^{20} 1.5335 68.67 5.81 3.80 8.79
66	137	$\text{CH}_3 > \text{CH} -$ CH_3			d	$\text{C}_{23}\text{H}_{25}\text{O}_2$ C: 82.10 H: 8.39	n_D^{20} 1.5299 82.15 8.30
67	138	$\text{CH}_3 > \text{CH} -$ CH_3			d	$\text{C}_{22}\text{H}_{25}\text{O}_2\text{Cl}$ C: 74.04 H: 7.06 Cl: 9.94	n_D^{20} 1.5414 74.08 7.10 10.03
68	139	$\text{CH}_3 > \text{CH} -$ CH_3			b	$\text{C}_{19}\text{H}_{17}\text{O}_2\text{Cl}_5$ C: 50.19 H: 3.77 Cl: 39.01	n_D^{20} 1.5382 50.22 3.79 39.13
69	140	$\text{CH}_3 > \text{CH} -$ CH_3			a	$\text{C}_{20}\text{H}_{17}\text{O}_2\text{FCl}_2$ C: 63.34 H: 4.52 F: 5.01 Cl: 18.70	n_D^{20} 1.5288 63.39 4.46 5.08 18.80

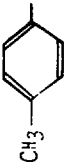
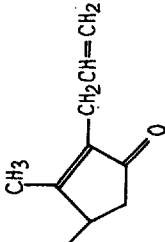
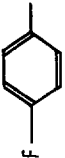
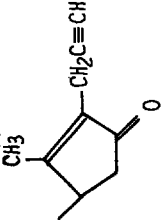
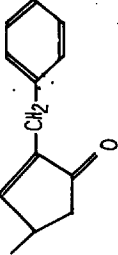
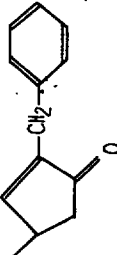
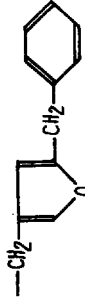
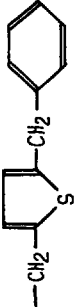
PREPARATIVE TABLE

Preparation Exp. No.	Comp. No.	Z	Y	X	Esteri- fication Yield Method (%)	Physical Formula Calcd. (%)	Properties Refractive Index Found (%)
70	141	$\text{CH}_3 > \text{CH}-$ CH_3			a	$\text{C}_{12}\text{H}_{10}\text{O}_2\text{F}_3$ C: 70.76 H: 5.40 F: 15.27	n_D^{20} 1.5385 70.80 5.39 15.27
71	142	$\text{CH}_3 > \text{CH}-$ CH_3			a	$\text{C}_{22}\text{H}_{16}\text{O}_2$ C: 81.95 H: 8.13	n_D^{20} 1.5236 82.06 8.12
72	143	$\text{CH}_3 > \text{CH}-$ CH_3			a	$\text{C}_{14}\text{H}_{10}\text{O}_2$ C: 82.24 H: 8.63	n_D^{20} 1.5341 82.19 8.66
73	144	$\text{CH}_3 > \text{CH}-$ CH_3			a	$\text{C}_{11}\text{H}_{13}\text{O}_2\text{Cl}$ C: 73.56 H: 6.76 Cl: 10.34	n_D^{20} 1.5491 73.51 6.81 10.29
74	145	$\text{CH}_3 > \text{CH}-$ CH_3			b	$\text{C}_{22}\text{H}_{14}\text{O}_3\text{S}$ C: 71.71 H: 6.56 S: 8.70	n_D^{20} 1.5372 71.73 6.60 8.79
75	146	$\text{CH}_3 > \text{CH}-$ CH_3			a	$\text{C}_{21}\text{H}_{14}\text{O}_3$ C: 77.75 H: 7.46	n_D^{20} 1.5377 77.77 7.40

PREPARATIVE TABLE

Preparation Exp. No.	Comp. No.	Z	Y	X	Esteri- fication Method (%)	Physical Formula Calcd. (%)	Properties Refractive Index Found (%)
76	147	$\text{CH}_3 > \text{CH}-$ CH_3			a	$\text{C}_{18}\text{H}_{20}\text{O}_4\text{NCl}$ C: 61.80 H: 5.76 N: 4.01 Cl: 10.14	n_D^{20} 1.5469 61.90 5.73 4.02 10.19
77	148	$\text{CH}_3 > \text{CH}-$ CH_3			b	$\text{C}_{22}\text{H}_{25}\text{O}_2\text{Cl}$ C: 74.04 H: 7.06 Cl: 9.94	n_D^{20} 1.5471 74.11 7.92 9.90
78	149	$\text{CH}_3 > \text{CH}-$ CH_3			a	$\text{C}_{23}\text{H}_{26}\text{O}_2\text{Cl}$ C: 74.68 H: 7.09 Cl: 9.59	n_D^{20} 1.5483 74.77 7.12 9.52
79	150	$\text{CH}_3 > \text{CH}-$ CH_3			a	$\text{C}_{21}\text{H}_{26}\text{O}_2\text{S}$ C: 73.64 H: 7.65 S: 9.36	n_D^{20} 1.5396 73.66 7.64 9.50
80	151	$\text{CH}_3 > \text{CH}-$ CH_3			a	$\text{C}_{21}\text{H}_{21}\text{O}_2\text{Cl}$ C: 74.00 H: 6.21 Cl: 10.40	n_D^{20} 1.5611 74.11 6.23 10.36
81	152	$\text{CH}_3 > \text{CH}-$ CH_3			e	$\text{C}_{20}\text{H}_{22}\text{O}_4\text{NF}$ C: 66.84 H: 6.17 N: 3.90 F: 5.29	n_D^{20} 1.5229 66.88 6.18 4.01 5.30

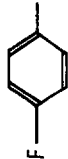
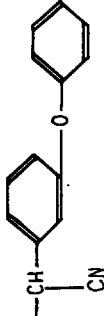
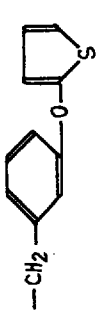
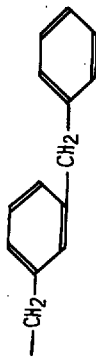
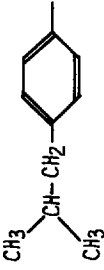
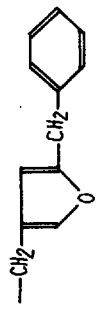
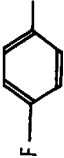
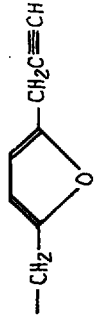
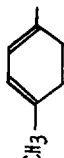
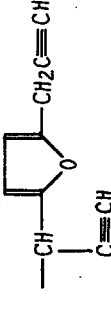
PREPARATIVE TABLE

Preparation Exp. No.	Comp. No.	Z	Y	X	Esteri- fication Method (%)	Physical Formula Calcd. (%)	Properties Refractive Index Found (%)
82	153	$\text{CH}_3 > \text{CH} -$ CH_3			b	$\text{C}_{21}\text{H}_{26}\text{O}_3$ C: 77.27 H: 8.03	n_D^{20} 1.5387 77.20 8.09
83	154	$\text{CH}_3 > \text{CH} -$ CH_3			a	$\text{C}_{20}\text{H}_{24}\text{O}_3\text{F}$ C: 73.15 H: 6.45 F: 5.79	n_D^{20} 1.5316 73.19 6.50 5.81
84	155	$\text{CH}_3 > \text{CH} -$ CH_3			a	$\text{C}_{24}\text{H}_{26}\text{O}_3$ C: 79.53 H: 7.23	n_D^{20} 1.5452 79.55 7.33
85	156	$\text{CH}_3 > \text{CH} -$ CH_3			a	$\text{C}_{23}\text{H}_{23}\text{O}_3\text{Cl}$ C: 72.15 H: 6.05 Cl: 9.26	n_D^{20} 1.5448 72.18 6.00 9.32
86	157	$\text{CH}_3 > \text{CH} -$ CH_3			a	$\text{C}_{23}\text{H}_{23}\text{O}_3\text{I}$ C: 58.24 H: 4.89 I: 26.76	n_D^{20} 1.5352 58.22 4.93 26.88
87	158	$\text{CH}_3 > \text{CH} -$ CH_3			a	$\text{C}_{24}\text{H}_{26}\text{O}_3\text{S}$ C: 76.15 H: 6.92 S: 8.47	n_D^{19} 1.5311 76.16 7.03 8.46

PREPARATIVE TABLE

Preparation Exp. No.	Comp. No.	Z	Y	X	Esteri- fication Method (%)	Physical Formula Calcd. (%)	Properties Refractive Index Found (%)
88	159	$\text{CH}_3 > \text{CH} -$ CH_3			a	$\text{C}_{16}\text{H}_{20}\text{O}_2\text{S}$ C: 76.80 H: 7.44 S: 7.89	n_D^{20} 1.5342 76.77 7.51 7.82
89	160	$\text{CH}_3 > \text{CH} -$ CH_3			a	$\text{C}_{22}\text{H}_{22}\text{O}_3$ C: 79.01 H: 6.63	n_D^{20} 1.5262 79.22 6.58
90	161	$\text{CH}_3 > \text{CH} -$ CH_3			a	$\text{C}_{23}\text{H}_{24}\text{O}_3$ C: 79.28 H: 6.94	n_D^{22} 1.5291 79.33 7.10
91	162	$\text{CH}_3 > \text{CH} -$ CH_3			a	$\text{C}_{22}\text{H}_{26}\text{O}_2$ C: 81.95 H: 8.13	n_D^{20} 1.5366 82.00 8.18
92	163	$\text{CH}_3 > \text{CH} -$ CH_3			a	$\text{C}_{26}\text{H}_{20}\text{O}_5\text{S}$ C: 73.90 H: 7.16 S: 7.59	n_D^{20} 1.5361 73.92 7.17 7.63
93	164	$\text{CH}_3 > \text{CH} -$ CH_3			a	$\text{C}_{22}\text{H}_{22}\text{O}_2\text{SF}$ C: 68.73 H: 5.51 S: 8.34 F: 4.94	n_D^{20} 1.4837 68.77 5.48 8.36 4.90

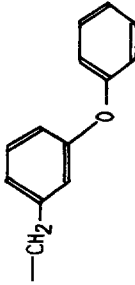
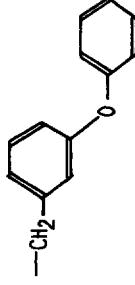
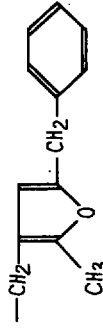
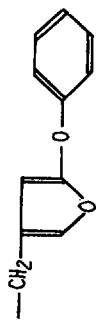
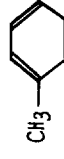
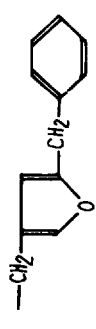
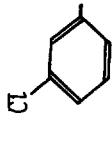
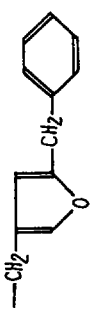
PREPARATIVE TABLE

Preparation Exp. No.	Comp. No.	Z	Y	X	Esteri- fication Method (%)	Yield (%)	Physical Formula Calcd. (%)	Properties Refractive Index Found (%)
94	165	$\text{CH}_3 > \text{CH} -$ CH_3			a	88	$\text{C}_{25}\text{H}_{22}\text{O}_3\text{NF}$ C: 74.42 H: 5.50 N: 3.47 F: 4.71	n_D^{20} 1.5233 74.49 5.56 3.49 4.79
95	166	$\text{CH}_3 > \text{CH} -$ CH_3			a	92	$\text{C}_{22}\text{H}_{21}\text{O}_3\text{SBr}$ C: 59.33 H: 4.75 S: 7.20 Br: 17.94	n_D^{20} 1.5811 59.36 4.79 7.11 17.92
96	167	$\text{CH}_3 > \text{CH} -$ CH_3			d	91	$\text{C}_{25}\text{H}_{23}\text{O}_2\text{Br}$ C: 68.97 H: 5.32 Br: 18.36	n_D^{20} 1.5802 68.96 5.33 18.40
97	168	$\text{CH}_3 > \text{CH} -$ CH_3			a	93	$\text{C}_{27}\text{H}_{32}\text{O}_3$ C: 80.16 H: 7.97	n_D^{20} 1.5387 80.15 7.96
98	169	$\text{C}_2\text{H}_5 -$			a	79	$\text{C}_{18}\text{H}_{17}\text{O}_3\text{F}$ C: 71.98 H: 5.71 F: 6.33	n_D^{20} 1.5218 71.99 5.76 6.27
99	170	$\text{C}_2\text{H}_5 -$			b	82	$\text{C}_{21}\text{H}_{20}\text{O}_3$ C: 78.72 H: 6.29	n_D^{20} 1.5261 78.77 6.22

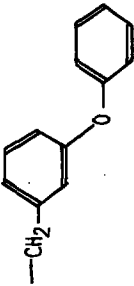
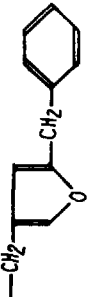
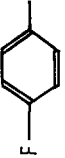
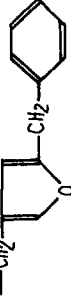
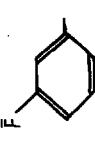
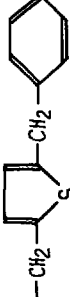
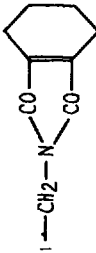
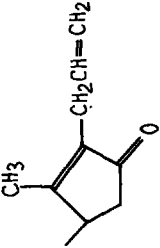
PREPARATIVE TABLE

Preparation Exp. No.	Comp. No.	Z	Y	X	Esteri- fication Method (%)	Physical Formula Calcd. (%)	Properties Refractive Index Found (%)
100	171	C ₂ H ₅ —			e	C ₂₆ H ₂₀ O ₃ C: 80.38 H: 7.27	n _D ¹⁹ 1.5536 80.29 7.33
101	172	C ₂ H ₅ —			e	C ₂₂ H ₂₂ O ₃ S C: 72.10 H: 6.05 S: 8.75	n _D ¹⁹ 1.5499 72.16 6.07 8.82
102	173	C ₂ H ₅ —			a	C ₂₀ H ₂₁ O ₂ Cl C: 73.05 H: 6.44 Cl: 10.78	n _D ²⁰ 1.5236 73.09 6.46 10.69
103	174	C ₂ H ₅ —			a	C ₂₁ H ₂₂ O ₂ C: 82.32 H: 7.24	n _D ²⁰ 1.5252 82.40 7.26
104	175	C ₂ H ₅ —			a	C ₂₀ H ₁₉ O ₄ Br C: 59.56 H: 4.75 Br: 19.82	n _D ²⁰ 1.5233 59.61 4.77 20.91
105	176	C ₂ H ₅ —			e	C ₂₄ H ₂₄ O ₃ C: 79.97 H: 6.71	n _D ²⁰ 1.5711 80.05 6.77

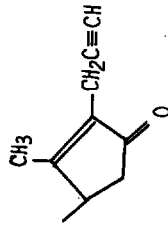
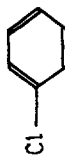
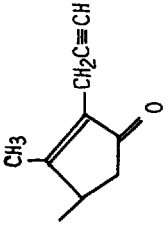
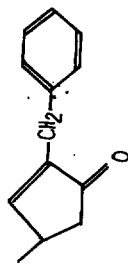
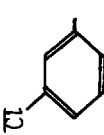
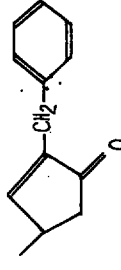
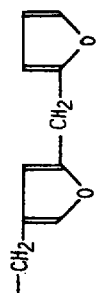
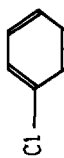
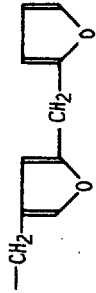
PREPARATIVE TABLE

Preparation Exp. No.	Comp. No.	Z	Y	X	Esteri- fication Method (%)	Physical Formula Calcd. (%)	Properties Refractive Index Found (%)
106	177	C ₂ H ₅ —			e	C ₂₃ H ₂₁ O ₃ Cl C: 72.53 H: 5.56 Cl: 9.31	n _D ²⁵ 1.5732 72.51 5.46 9.33
107	178	C ₂ H ₅ —			e	C ₂₃ H ₂₁ O ₃ Br C: 64.95 H: 4.98 Br: 18.79	n _D ¹⁷ 1.5861 64.92 4.86 18.82
108	179	C ₂ H ₅ —			a	C ₂₃ H ₂₃ O ₃ I C: 58.24 H: 4.89 I: 26.76	n _D ²⁰ 1.5733 58.25 4.92 28.81
109	180	C ₂ H ₅ —			b	C ₂₁ H ₁₉ O ₃ Cl C: 68.01 H: 5.16 Cl: 9.56	n _D ²⁰ 1.5625 66.06 5.22 9.62
110	181	CH ₃ —			a	C ₂₂ H ₂₂ O ₃ C: 79.01 H: 6.63	n _D ²⁵ 1.5471 79.07 6.58
111	182	CH ₃ —			a	C ₂₁ H ₁₉ O ₃ Cl C: 71.08 H: 5.40 Cl: 9.99	n _D ²² 1.5518 71.11 5.32 9.89

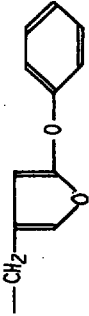
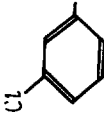
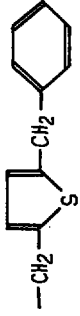
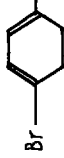
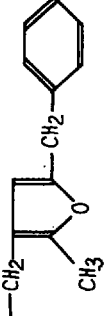
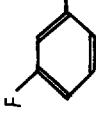
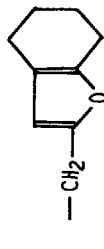
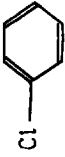
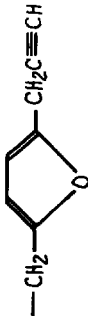
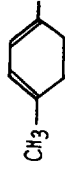
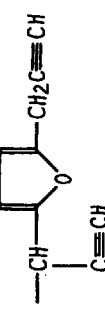
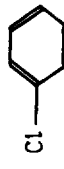
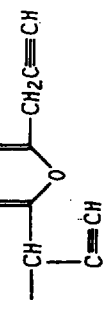
PREPARATIVE TABLE

Preparation Exp. No.	Comp. No.	Z	Y	X	Esteri- fication Method	Yield (%)	Physical Formula Calcd. (%)	Properties Refractive Index Found (%)
112	183	CH ₃ —			e	87	C ₂₃ H ₂₂ O ₃ C: 79.74 H: 6.40	n _D ²⁵ 1.5592 79.77 6.36
113	184	C ₂ H ₅ —			a	88	C ₂₃ H ₂₁ O ₃ Cl C: 71.63 H: 5.74 Cl: 9.61	n _D ²⁵ 1.5549 71.66 5.81 9.70
114	185	C ₂ H ₅ —			a	87	C ₂₂ H ₂₁ O ₃ F C: 74.98 H: 6.00 F: 5.39	n _D ²⁰ 1.4437 75.03 6.02 5.29
115	186	C ₂ H ₅ —			a	83	C ₂₂ H ₂₁ O ₃ SF C: 71.71 H: 5.75 S: 8.70 F: 5.16	n _D ²⁰ 1.4933 71.77 5.76 8.81 5.13
116	187	C ₂ H ₅ —			e	76	C ₁₉ H ₂₀ O ₂ NCl C: 63.07 H: 5.57 N: 3.87 Cl: 9.80	n _D ²⁰ 1.5316 62.98 5.54 3.92 9.69
117	188	C ₂ H ₅ —			a	83	C ₂₀ H ₂₄ O ₃ C: 76.89 H: 7.74	n _D ²⁰ 1.5224 76.79 7.81

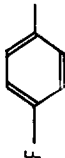
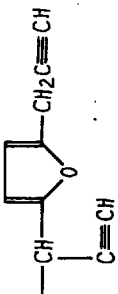
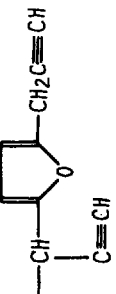
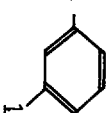
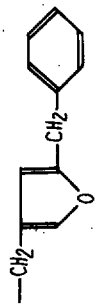
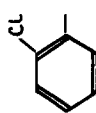
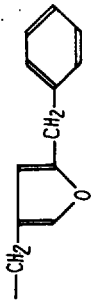
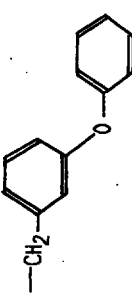
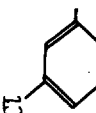
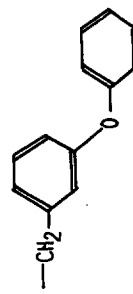
PREPARATIVE TABLE

Preparation Exp. No.	Comp. No.	Z	Y	X	Esteri- fication Method (%)	Yield (%)	Physical Formula Calcd. (%)	Properties Refractive Index Found (%)
118	189	C_2H_5-			a	80	$C_{20}H_{22}O_3$ C: 77.39 H: 7.14	n_D^{20} 1.5456 77.44 7.14
119	190	C_2H_5-			a	82	$C_{19}H_{19}O_3Cl$ C: 68.98 H: 5.79 Cl: 10.72	n_D^{20} 1.5445 68.92 5.78 10.85
120	191	C_2H_5-			a	90	$C_{22}H_{21}O_3F$ C: 74.98 H: 6.01 F: 5.39	n_D^{20} 1.5267 74.87 6.02 5.41
121	192	C_2H_5-			a	92	$C_{22}H_{21}O_3Cl$ C: 71.63 H: 5.74 Cl: 9.61	n_D^{20} 1.5352 71.66 5.78 9.62
122	193	$\begin{matrix} CH_3 \\ >CH- \\ CH_3 \end{matrix}$			a	90	$C_{22}H_{24}O_4$ C: 74.97 H: 6.86	n_D^{19} 1.5377 75.10 6.86
123	194	$\begin{matrix} CH_3 \\ >CH- \\ CH_3 \end{matrix}$			a	91	$C_{21}H_{21}O_4Cl$ C: 67.65 H: 5.68 Cl: 9.51	n_D^{19} 1.5421 67.62 5.72 9.61

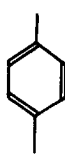
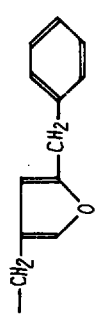
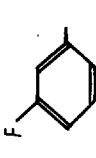
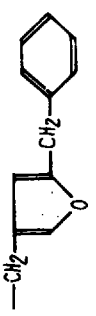
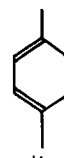
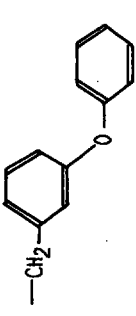
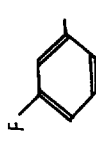
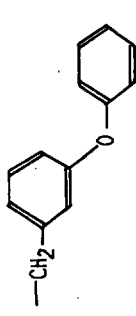
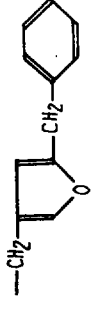
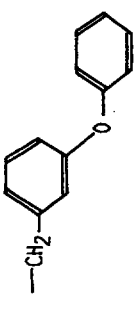
PREPARATIVE TABLE

Preparation Exp. No.	Comp. No.	Z	Y	X	Esteri- fication Method (%)	Yield (%)	Physical Formula Calcd. (%)	Properties Refractive Index Found (%)
124	195	$\text{CH}_3 > \text{CH} -$ CH_3			a	89	$\text{C}_{23}\text{H}_{22}\text{O}_4$ C: 75.80 H: 6.64	n_D^{20} 1.5235 75.83 6.70
125	196	$\text{CH}_3 > \text{CH} -$ CH_3			a	91	$\text{C}_{23}\text{H}_{23}\text{O}_2\text{S}$ C: 69.24 H: 5.81 S: 8.04	n_D^{20} 1.5551 69.26 5.84 8.11
126	197	$\text{CH}_3 > \text{CH} -$ CH_3			a	88	$\text{C}_{24}\text{H}_{23}\text{O}_2\text{Br}$ C: 65.31 H: 5.71 Br: 18.11	n_D^{20} 1.5349 65.33 5.83 18.20
127	198	$\text{CH}_3 > \text{CH} -$ CH_3			a	92	$\text{C}_{20}\text{H}_{23}\text{O}_3\text{F}$ C: 72.70 H: 7.02 F: 5.75	n_D^{20} 1.5466 72.69 7.11 5.72
128	199	$\text{CH}_3 > \text{CH} -$ CH_3			a	80	$\text{C}_{19}\text{H}_{19}\text{O}_3\text{Cl}$ C: 68.98 H: 5.79 Cl: 10.72	n_D^{19} 1.5238 69.01 5.72 10.77
129	200	$\text{CH}_3 > \text{CH} -$ CH_3			a	82	$\text{C}_{22}\text{H}_{22}\text{O}_3$ C: 79.01 H: 6.63	n_D^{20} 1.5265 79.10 6.58
130	201	$\text{CH}_3 > \text{CH} -$ CH_3			a	79	$\text{C}_{21}\text{H}_{19}\text{O}_3\text{Cl}$ C: 71.08 H: 5.40 Cl: 9.99	n_D^{20} 1.5233 71.00 5.46 9.89

PREPARATIVE TABLE

Preparation Exp. No.	Comp. No.	Z	Y	X	Esteri- fication Method (%)	Yield (%)	Physical Formula Calcd. (%)	Properties Refractive Index Found (%)
131	202	$\text{CH}_3 > \text{CH} -$ CH_3			a	75	$\text{C}_{21}\text{H}_{19}\text{O}_3\text{F}$ C: 74.54 H: 5.66 F: 5.62	n_D^{20} 1.5249 74.53 5.77 5.66
132	203	$\text{CH}_3 > \text{CH} -$ CH_3			a	83	$\text{C}_{21}\text{H}_{19}\text{O}_3\text{Br}$ C: 63.17 H: 4.80 Br: 20.02	n_D^{20} 1.5289 63.18 4.79 20.04
133	204	$\text{CH}_3 > \text{CH} -$ CH_3			a	90	$\text{C}_{23}\text{H}_{23}\text{O}_3\text{Cl}$ C: 72.15 H: 6.05 Cl: 9.26	n_D^{21} 1.5521 72.16 6.11 9.39
134	205	$\text{CH}_3 > \text{CH} -$ CH_3			a	89	$\text{C}_{23}\text{H}_{23}\text{O}_3\text{Cl}$ C: 72.15 H: 6.05 Cl: 9.26	n_D^{21} 1.5576 72.14 6.09 9.31
135	206	$\text{CH}_3 > \text{CH} -$ CH_3			d	83	$\text{C}_{24}\text{H}_{23}\text{O}_3\text{Cl}$ C: 72.99 H: 5.87 Cl: 8.98	n_D^{21} 1.5655 73.04 5.87 8.99
136	207	$\text{CH}_3 > \text{CH} -$ CH_3			e	92	$\text{C}_{24}\text{H}_{23}\text{O}_3\text{Cl}$ C: 72.99 H: 5.87 Cl: 8.98	n_D^{21} 1.5722 72.93 5.89 9.00

PREPARATIVE TABLE

Preparation Exp. No.	Comp. No.	Z	Y	X	Esteri- fication Method (%)	Physical Formula Calcd. (%)	Properties Refractive Index Found (%)
137	208	$\text{CH}_3 > \text{CH}-$ CH_3			d	$\text{C}_{23}\text{H}_{23}\text{O}_3\text{F}$ C: 75.39 H: 6.33 F: 5.19	n_D^{21} 1.4537 75.42 6.31 5.22
138	209	$\text{CH}_3 > \text{CH}-$ CH_3			a	$\text{C}_{23}\text{H}_{23}\text{O}_3\text{F}$ C: 75.39 H: 6.33 F: 5.19	n_D^{21} 1.5330 75.44 6.26 5.14
139	210	$\text{CH}_3 > \text{CH}-$ CH_3			d	$\text{C}_{24}\text{H}_{23}\text{O}_3\text{F}$ C: 76.17 H: 6.15 F: 5.02	n_D^{23} 1.5544 76.20 6.14 5.10
140	211	$\text{CH}_3 > \text{CH}-$ CH_3			e	$\text{C}_{24}\text{H}_{23}\text{O}_3\text{F}$ C: 76.17 H: 6.13 F: 5.02	$n_D^{21.5}$ 1.5543 76.15 6.13 5.11
141	212	$\text{CH}_3 > \text{CH}-$ CH_3			a	$\text{C}_{24}\text{H}_{23}\text{O}_3\text{Br}$ C: 64.64 H: 5.42 Br: 18.70	n_D^{17} 1.5651 64.58 5.44 18.96
142	213	$\text{CH}_3 > \text{CH}-$ CH_3			e	$\text{C}_{24}\text{H}_{23}\text{O}_3\text{Br}$ C: 65.61 H: 5.28 Br: 18.19	$n_D^{17.5}$ 1.5802 65.62 5.30 18.23

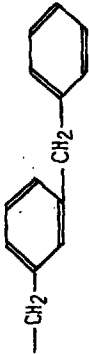
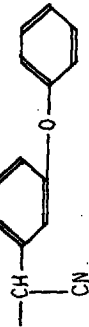
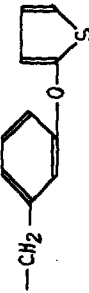
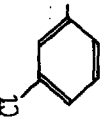
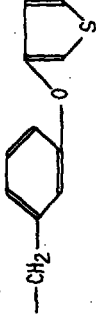
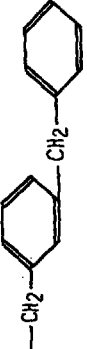
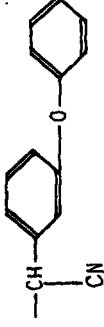
PREPARATIVE TABLE

Preparation Exp. No.	Comp. No.	Z	Y	X	Esteri- fication Yield Method (%)	Physical Formula Calcd. (%)	Properties Refractive Index Found (%)
143	214	$\text{CH}_3 > \text{CH} -$ CH_3			a	$\text{C}_{25}\text{H}_{20}\text{O}_3$ C: 79.75 H: 7.50	$n_D^{18.5}$ 1.5347 79.81 7.51
144	215	$\text{CH}_3 > \text{CH} -$ CH_3			a	$\text{C}_{26}\text{H}_{20}\text{O}_3$ C: 80.38 H: 7.27	$n_D^{21.5}$ 1.5590 80.34 7.29
145	216	$\text{CH}_3 > \text{CH} -$ CH_3			a	$\text{C}_{26}\text{H}_{20}\text{O}_3$ C: 79.96 H: 7.74	n_D^{18} 1.5387 80.01 7.70
146	217	$\text{CH}_3 > \text{CH} -$ CH_3			a	$\text{C}_{27}\text{H}_{20}\text{O}_3$ C: 80.56 H: 7.51	n_D^{18} 1.5542 80.52 7.52
147	218	$\text{CH}_3 > \text{CH} -$ CH_3			a	$\text{C}_{26}\text{H}_{20}\text{O}_3$ C: 79.96 H: 7.74	n_D^{22} 1.5385 79.94 7.83
148	219	$\text{CH}_3 > \text{CH} -$ CH_3			a	$\text{C}_{27}\text{H}_{20}\text{O}_3$ C: 80.56 H: 7.51	n_D^{19} 1.5548 80.58 7.53

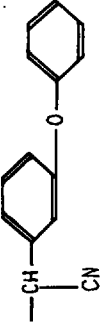
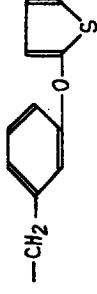
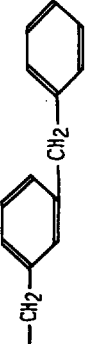
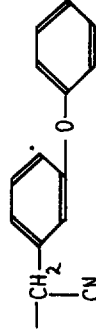
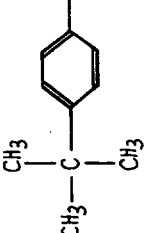
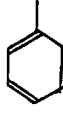
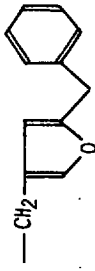
PREPARATIVE TABLE

Preparation Exp. No.	Comp. No.	Z	Y	X	Esteri- fication Yield Method (%)	Physical Formula Calcd. (%)	Properties Refractive Index Found (%)
149	220	$\text{CH}_3 > \text{CH} -$ CH_3			a	$\text{C}_{27}\text{H}_{32}\text{O}_3$ C: 80.16 H: 7.97	n_D^{25} 1.5302 80.21 8.04
150	221	$\text{CH}_3 > \text{CH} -$ CH_3			a	$\text{C}_{28}\text{H}_{32}\text{O}_3$ C: 80.73 H: 7.74	n_D^{25} 1.5327 80.67 7.71
151	222	$\text{CH}_3 > \text{CH} -$ CH_3			a	$\text{C}_{21}\text{H}_{21}\text{O}_3\text{SCl}$ C: 64.85 H: 5.44 S: 8.25 Cl: 9.12	n_D^{25} 1.5377 64.88 5.42 8.26 9.13
152	223	$\text{CH}_3 > \text{CH} -$ CH_3			a	$\text{C}_{22}\text{H}_{21}\text{O}_3\text{SF}$ C: 68.73 H: 5.51 S: 8.34 F: 4.94	n_D^{25} 1.5467 68.70 5.59 8.32 4.92
153	224	$\text{CH}_3 > \text{CH} -$ CH_3			a	$\text{C}_{23}\text{H}_{24}\text{O}_3\text{S}$ C: 72.60 H: 6.36 S: 8.43	n_D^{25} 1.5366 72.54 6.33 8.50
154	225	$\text{CH}_3 > \text{CH} -$ CH_3			a	$\text{C}_{23}\text{H}_{24}\text{O}_3\text{S}$ C: 72.60 H: 6.36 S: 8.43	n_D^{25} 1.5277 72.61 6.38 8.49

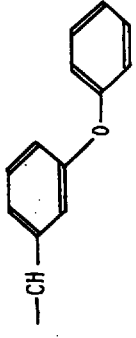
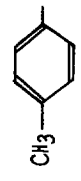
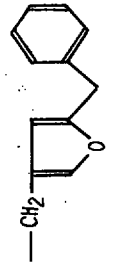
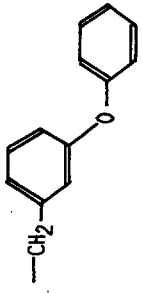
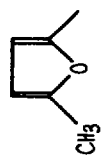
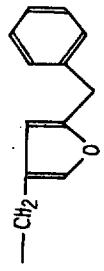
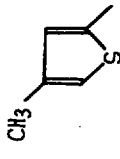
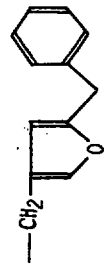
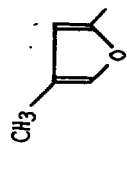
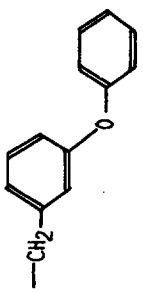
PREPARATIVE TABLE

Preparation Exp. No.	Comp. No.	Z	Y	X	Esteri- fication Method (%)	Physical Formula Calcd. (%)	Properties Refractive Index Found (%)
155	226	$\text{CH}_3 > \text{CH}-$ CH_3			a	$\text{C}_{26}\text{H}_{28}\text{O}_2$ C: 81.62 H: 10.01	n_D^{20} 1.5235 81.66 10.03
156	227	$\text{CH}_3 > \text{CH}-$ CH_3			a	$\text{C}_{26}\text{H}_{23}\text{O}_3\text{N}$ C: 78.17 H: 6.31 N: 3.51	n_D^{20} 1.5624 78.19 6.28 3.61
157	228	$\text{CH}_3 > \text{CH}-$ CH_3			a	$\text{C}_{22}\text{H}_{21}\text{O}_3\text{SCl}$ C: 65.90 H: 5.28 S: 8.00 Cl: 8.84	n_D^{19} 1.5433 65.99 5.27 8.04 8.82
158	229	$\text{CH}_3 > \text{CH}-$ CH_3			a	$\text{C}_{22}\text{H}_{21}\text{O}_3\text{SCl}$ C: 65.90 H: 5.28 S: 8.00 Cl: 8.84	n_D^{19} 1.5436 65.91 5.29 8.16 8.83
159	230	$\text{CH}_3 > \text{CH}-$ CH_3			a	$\text{C}_{23}\text{H}_{25}\text{O}_2\text{Cl}$ C: 76.42 H: 6.41 Cl: 9.02	n_D^{20} 1.5329 76.44 6.43 9.09
160	231	$\text{CH}_3 > \text{CH}-$ CH_3			a	$\text{C}_{23}\text{H}_{22}\text{O}_2\text{NCl}$ C: 71.51 H: 5.28 N: 3.34 Cl: 8.44	n_D^{20} 1.5533 71.54 5.30 3.31 8.46

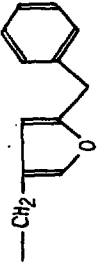
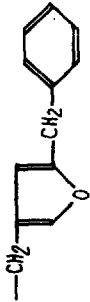
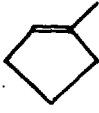
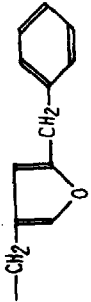
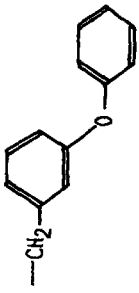
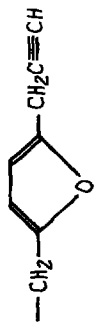
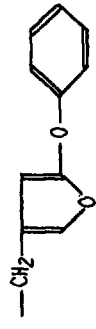
PREPARATIVE TABLE

Preparation Exp. No.	Comp. No.	Z	Y	X	Esteri- fication Yield (%) Method	Physical Formula Calcd. (%)	Properties Refractive Index Found (%)
161	232	$\text{CH}_3 > \text{CH} - \text{CH}_3$			a	$\text{C}_{17}\text{H}_{17}\text{O}_3\text{N}$ C: 78.42 H: 6.58 N: 3.39	n_D^{20} 1.5239 78.44 6.61 3.44
162	233	$\text{CH}_3 > \text{CH} - \text{CH}_3$			a	$\text{C}_{23}\text{H}_{28}\text{O}_3\text{S}$ C: 73.49 H: 6.91 S: 7.85	n_D^{20} 1.5567 73.51 6.94 7.86
163	234	$\text{CH}_3 > \text{CH} - \text{CH}_3$			a	$\text{C}_{28}\text{H}_{28}\text{O}_2$ C: 83.96 H: 8.05	n_D^{20} 1.5341 83.99 8.06
164	235	$\text{CH}_3 > \text{CH} - \text{CH}_3$			a	$\text{C}_{28}\text{H}_{29}\text{O}_3\text{N}$ C: 78.66 H: 6.84 N: 3.28	n_D^{20} 1.5226 78.67 6.90 3.11
165	236	$\text{CH}_3 > \text{CH} - \text{CH}_3$			a	$\text{C}_{28}\text{H}_{29}\text{O}_3\text{N}$ C: 78.88 H: 7.08 N: 3.17	n_D^{20} 1.5451 78.79 7.06 3.24
166	237	$\text{CH}_3 > \text{CH} - \text{CH}_3$			a	$\text{C}_{24}\text{H}_{26}\text{O}_3$ C: 79.53 H: 7.23	n_D^{20} 1.5335 79.56 7.20

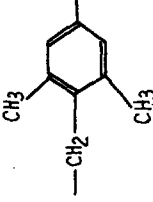
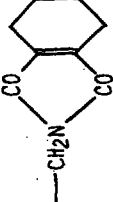
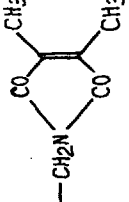
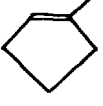
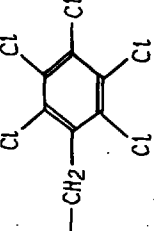
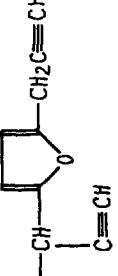
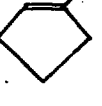
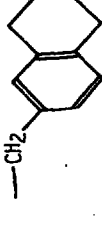
PREPARATIVE TABLE

Preparation Exp. No.	Comp. No.	Z	Y	X	Esteri- fication Method (%)	Yield (%)	Physical Formula Calcd. (%)	Properties Refractive Index Found (%)
167	238	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{C} - \text{CH}_3 \\ \\ \text{CH}_3 \end{array}$			a	89	$\text{C}_{11}\text{H}_{13}\text{O}_3\text{Cl}$ C: 73.43 H: 6.16 Cl: 8.67	n_D^{20} 1.5427 73.49 6.20 8.60
168	239	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{C} - \text{CH}_3 \\ \\ \text{CH}_3 \end{array}$			a	89	$\text{C}_{11}\text{H}_{13}\text{O}_3$ C: 79.75 H: 7.49	n_D^{20} 1.5366 79.72 7.52
169	240	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{C} - \text{CH}_3 \\ \\ \text{CH}_3 \end{array}$			a	91	$\text{C}_{16}\text{H}_{23}\text{O}_3$ C: 80.38 H: 7.26	n_D^{21} 1.5225 80.33 7.24
170	241	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 > \text{CH} - \end{array}$			a	76	$\text{C}_{23}\text{H}_{24}\text{O}_4$ C: 74.98 H: 6.86	n_D^{22} 1.5236 75.02 6.80
171	242	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 > \text{CH} - \end{array}$			a	79	$\text{C}_{23}\text{H}_{24}\text{O}_3\text{S}$ C: 71.71 H: 6.56 S: 8.70	n_D^{20} 1.5475 71.77 6.52 8.72
172	243	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 > \text{CH} - \end{array}$			a	79	$\text{C}_{23}\text{H}_{24}\text{O}_4$ C: 75.80 H: 6.64	n_D^{20} 1.5344 75.76 6.62

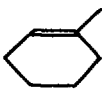
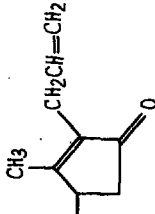
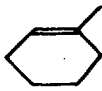
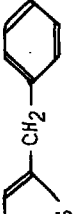
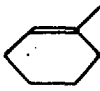
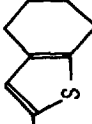
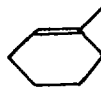
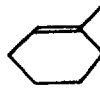
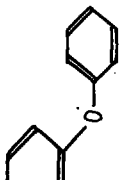
PREPARATIVE TABLE

Preparation Exp. No.	Comp. No.	Z	Y	X	Esteri- fication Method (%)	Physical Formula Calcd. (%)	Properties Refractive Index Found (%)
173	244	$\text{CH}_3 > \text{CH}-$ CH_3			a	$\text{C}_{11}\text{H}_{12}\text{O}_3\text{S}$ C: 71.15 H: 6.26 S: 9.04	n_D^{19} 1.5226 71.09 6.22 9.11
174	245	CH_3-			a	$\text{C}_{10}\text{H}_{12}\text{O}_3$ C: 77.37 H: 7.14	n_D^{28} 1.5293 77.29 7.16
175	246	C_2H_5			a	$\text{C}_{11}\text{H}_{14}\text{O}_3$ C: 77.75 H: 7.46	$n_D^{24.5}$ 1.5276 77.78 7.44
176	247	$\text{CH}_3 > \text{CH}-$ CH_3			a	$\text{C}_{13}\text{H}_{16}\text{O}_3$ C: 78.83 H: 7.48	n_D^{28} 1.5483 78.81 7.40
177	248	C_2H_5			a	$\text{C}_{18}\text{H}_{22}\text{O}_3$ C: 75.49 H: 7.74	$n_D^{24.5}$ 1.4965 75.53 7.69
178	249	$\text{CH}_3 > \text{CH}-$ CH_3			a	$\text{C}_{22}\text{H}_{26}\text{O}_3$ C: 78.07 H: 7.74	$n_D^{24.5}$ 1.5248 78.10 7.74

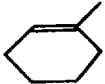
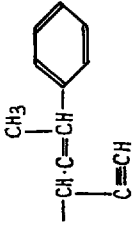
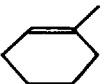
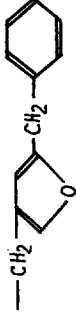
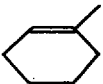
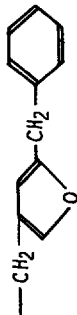
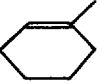
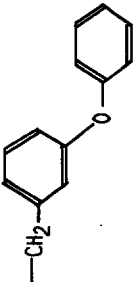
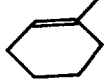
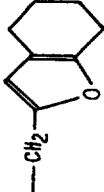
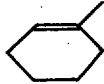
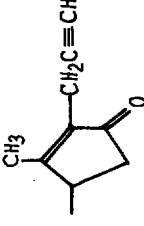
PREPARATIVE TABLE

Preparation Exp. No.	Comp. No.	Z	Y	X	Esteri- fication Yield Method (%)	Physical Formula Calcd. (%)	Properties Refractive Index Found (%)
179	250	$\text{CH}_3 > \text{CH}-$ CH_3			a	$\text{C}_{22}\text{H}_{25}\text{O}_2$ C: 81.44 H: 8.70	n_D^{25} 1.5615 81.64 8.53
180	251	$\text{CH}_3 > \text{CH}-$ CH_3			a	$\text{C}_{19}\text{H}_{25}\text{O}_4\text{N}$ C: 68.86 H: 7.60 N: 4.23	n_D^{25} 1.5380 68.69 7.64 4.10
181	252	$\text{CH}_3 > \text{CH}-$ CH_3			a	$\text{C}_{17}\text{H}_{23}\text{O}_4\text{N}$ C: 66.86 H: 7.59 N: 4.59	n_D^{25} 1.5237 66.97 7.50 4.45
182	253	$\text{CH}_3 > \text{CH}-$ CH_3			a	$\text{C}_{17}\text{H}_{17}\text{O}_2\text{Cl}_3$ C: 47.42 H: 3.98 Cl: 41.17	n_D^{25} 1.5395 47.88 3.70 41.53
183	254	$\text{CH}_3 > \text{CH}-$ CH_3			a	$\text{C}_{20}\text{H}_{22}\text{O}_2$ C: 77.37 H: 7.14	n_D^{25} 1.5088 77.35 7.17
184	255	$\text{CH}_3 > \text{CH}-$ CH_3			a	$\text{C}_{21}\text{H}_{25}\text{O}_2$ C: 80.73 H: 9.03	n_D^{25} 1.5132 80.70 8.98

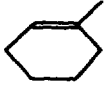
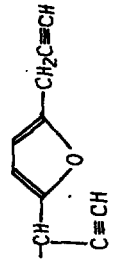
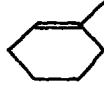
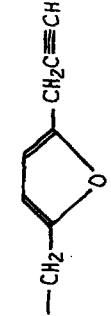
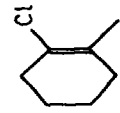
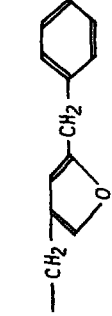
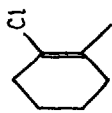
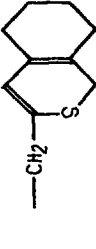
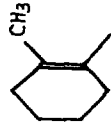
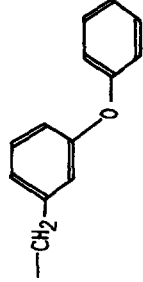
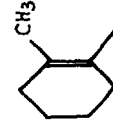
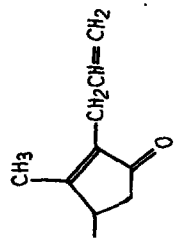
PREPARATIVE TABLE

Preparation Exp. No.	Comp. No.	Z	Y	X	Esteri- fication Method (%)	Physical Formula Calcd. (%)	Properties Refractive Index Found (%)
185	256	$\text{CH}_3 > \text{CH}-$ CH_3		$\text{---CH}_2\text{CH}=\text{C}(\text{Cl})\text{---CH}_2\text{---}$ 	a	$\text{C}_{20}\text{H}_{25}\text{O}_2\text{Cl}$ C: 72.16 H: 7.59 Cl: 10.65	n_D^{25} 1.5205 72.05 7.55 10.92
186	257	$\text{CH}_3 > \text{CH}-$ CH_3			a	$\text{C}_{20}\text{H}_{28}\text{O}_3$ C: 75.91 H: 8.92	$n_D^{24.5}$ 1.5085 75.86 8.90
187	258	$\text{CH}_3 > \text{CH}-$ CH_3		$\text{---CH}_2\text{---}$ 	a	$\text{C}_{23}\text{H}_{28}\text{O}_2\text{S}$ C: 74.96 H: 7.66 S: 8.70	n_D^{23} 1.5370 74.78 7.62 8.58
188	259	$\text{CH}_3 > \text{CH}-$ CH_3		$\text{---CH}_2\text{---}$ 	a	$\text{C}_{19}\text{H}_{26}\text{O}_2\text{S}$ C: 71.66 H: 8.23 S: 10.07	n_D^{23} 1.5352 71.69 8.24 9.80
189	260	$\text{CH}_3 > \text{CH}-$ CH_3		$\text{---CH}_2\text{---}$ 	a	$\text{C}_{19}\text{H}_{24}\text{O}_2\text{S}$ C: 72.11 H: 7.64 S: 10.13	n_D^{23} 1.5323 72.15 7.68 10.05
190	261	$\text{CH}_3 > \text{CH}-$ CH_3		---CH--- $\text{C}\equiv\text{N}$ 	a	$\text{C}_{23}\text{H}_{27}\text{O}_3\text{N}$ C: 77.09 H: 6.99 N: 3.60	n_D^{28} 1.5486 76.93 6.92 3.52

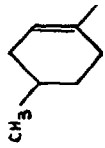
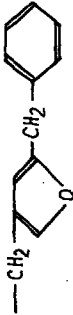
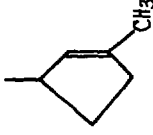
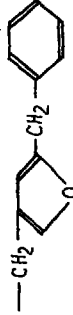
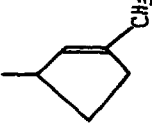
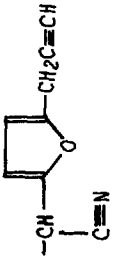
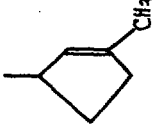
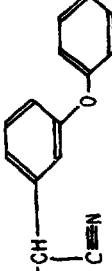
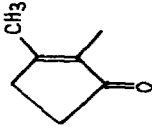
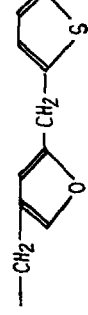
PREPARATIVE TABLE

Preparation Exp. No.	Comp. No.	Z	Y	X	Esteri- fication Yield Method (%)	Physical Formula Calcd. (%)	Properties Refractive Index Found (%)
191	262	$\text{CH}_3 > \text{CH}-$ CH_3			a	$\text{C}_{23}\text{H}_{26}\text{O}_2$ C: 82.10 H: 8.39	n_D^{25} 1.5213 82.15 8.39
192	263	CH_3-			a	$\text{C}_{21}\text{H}_{24}\text{O}_3$ C: 77.75 H: 7.46	n_D^{25} 1.5309 77.60 7.48
193	264	C_2H_5-			a	$\text{C}_{22}\text{H}_{26}\text{O}_3$ C: 78.07 H: 7.74	n_D^{25} 1.5308 78.12 7.61
194	265	$\text{CH}_3 > \text{CH}-$ CH_3			a	$\text{C}_{24}\text{H}_{28}\text{O}_3$ C: 79.09 H: 7.74	n_D^{25} 1.5467 78.80 7.76
195	266	C_2H_5-			a	$\text{C}_{19}\text{H}_{26}\text{O}_3$ C: 75.46 H: 8.67	n_D^{25} 1.5088 75.40 8.66
196	267	$\text{CH}_3 > \text{CH}-$ CH_3			a	$\text{C}_{20}\text{H}_{26}\text{O}_3$ C: 76.40 H: 8.34	n_D^{25} 1.5140 76.58 8.29

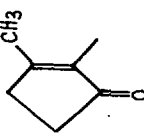
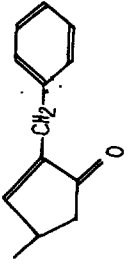
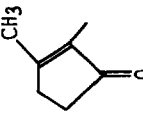
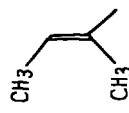
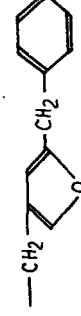
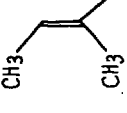
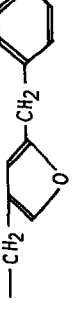
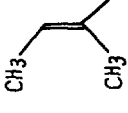
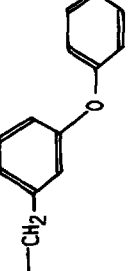
PREPARATIVE TABLE

Preparation Exp. No.	Comp. No.	Z	Y	X	Esteri- fication Method (%)	Physical Formula Calcd. (%)	Properties Refractive Index Found (%)
197	268	$\text{CH}_3 > \text{CH} -$ CH_3			a	$\text{C}_{21}\text{H}_{24}\text{O}_2$ C: 77.75 H: 7.46	$n_D^{24.5}$ 1.5133 77.81 7.40
198	269	$\text{CH}_3 > \text{CH} -$ CH_3			a	$\text{C}_{19}\text{H}_{24}\text{O}_2$ C: 75.97 H: 8.05	$n_D^{24.5}$ 1.5064 75.86 8.04
199	270	$\text{CH}_3 > \text{CH} -$ CH_3			a	$\text{C}_{21}\text{H}_{22}\text{O}_2\text{Cl}$ C: 70.86 H: 6.76 Cl: 9.51	$n_D^{24.5}$ 1.5358 70.66 6.73 9.30
200	271	$\text{CH}_3 > \text{CH} -$ CH_3			a	$\text{C}_{20}\text{H}_{22}\text{O}_2\text{ClS}$ C: 64.66 H: 7.14 Cl: 10.05 S: 9.09	n_D^{23} 1.5430 64.74 7.15 9.77 9.13
201	272	$\text{CH}_3 > \text{CH} -$ CH_3			a	$\text{C}_{23}\text{H}_{30}\text{O}_3$ C: 79.33 H: 7.99	n_D^{23} 1.5474 79.25 7.90
202	273	$\text{CH}_3 > \text{CH} -$ CH_3			a	$\text{C}_{21}\text{H}_{24}\text{O}_3$ C: 76.32 H: 9.15	n_D^{28} 1.5030 76.55 9.13

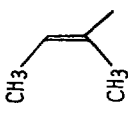
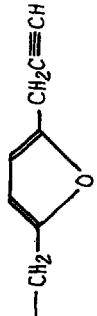
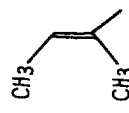
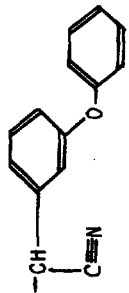
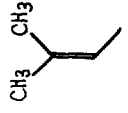
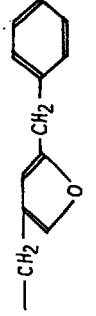
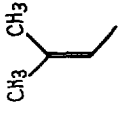
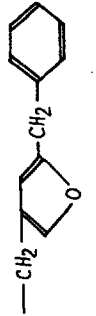
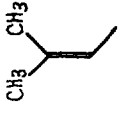
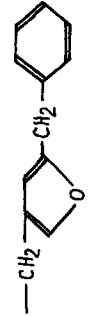
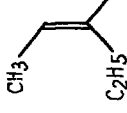
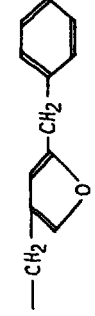
PREPARATIVE TABLE

Preparation Exp. No.	Comp. No.	Z	Y	X	Esteri- fication Method (%)	Physical Formula Calcd. (%)	Properties Refractive Index Found (%)
203	274	$\text{CH}_3 > \text{CH}-$ CH_3			a	$\text{C}_{24}\text{H}_{20}\text{O}_3$ C: 79.33 H: 7.99	n_D^{25} 1.5243 79.47 7.95
204	275	$\text{CH}_3 > \text{CH}-$ CH_3			a	$\text{C}_{23}\text{H}_{20}\text{O}_3$ C: 79.09 H: 7.74	n_D^{24} 1.5252 79.05 7.73
205	276	$\text{CH}_3 > \text{CH}-$ CH_3			a	$\text{C}_{20}\text{H}_{23}\text{O}_3\text{N}$ C: 77.75 H: 7.46	n_D^{24} 1.5097 77.62 7.49
206	277	$\text{CH}_3 > \text{CH}-$ CH_3			a	$\text{C}_{25}\text{H}_{27}\text{O}_3\text{N}$ C: 77.09 H: 6.99 N: 3.60	n_D^{25} 1.5470 77.11 6.80 3.53
207	278	$\text{CH}_3 > \text{CH}-$ CH_3			a	$\text{C}_{19}\text{H}_{20}\text{O}_4\text{S}$ C: 66.26 H: 5.85 S: 9.31	n_D^{25} 1.5335 66.07 5.88 9.24

PREPARATIVE TABLE

Preparation Exp. No.	Comp. No.	Z	Y	X	Esteri- fication Method (%)	Physical Formula Calcd. (%)	Properties Refractive Index Found (%)
208	279	$\text{CH}_3 > \text{CH}-$ CH_3			a	$\text{C}_{23}\text{H}_{36}\text{O}_4$ C: 75.38 H: 7.15	$n_D^{23} 1.5088$ 75.15 7.02
209	280	$\text{CH}_3 > \text{CH}-$ CH_3			a	$\text{C}_{23}\text{H}_{36}\text{O}_4$ C: 75.38 H: 7.15	$n_D^{23} 1.5075$ 75.36 7.18
210	281	C_2H_5-			a	$\text{C}_{20}\text{H}_{34}\text{O}_3$ C: 76.89 H: 7.74	$n_D^{28.5} 1.5178$ 76.54 7.70
211	282	$\text{CH}_3 > \text{CH}-$ CH_3			a	$\text{C}_{21}\text{H}_{36}\text{O}_3$ C: 77.27 H: 8.03	$n_D^{23} 1.5185$ 77.34 8.06
212	283	$\text{CH}_3 > \text{CH}-$ CH_3			a	$\text{C}_{22}\text{H}_{36}\text{O}_3$ C: 78.07 H: 7.74	$n_D^{23} 1.5413$ 77.95 7.90

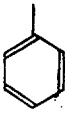
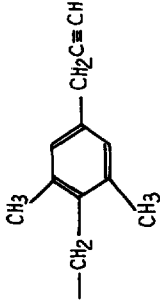
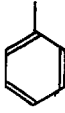
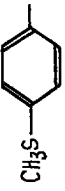
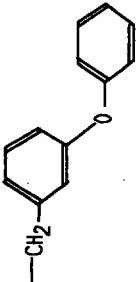
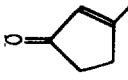
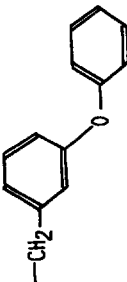
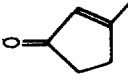
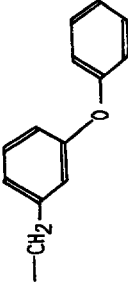
PREPARATIVE TABLE

Preparation Exp. No.	Comp. No.	Z	Y	X	Esteri- fication Method (%)	Physical Formula Calcd. (%)	Properties Refractive Index Found (%)
213	284	$\text{CH}_3 > \text{CH} - \text{CH}_3$			a	$\text{C}_{17}\text{H}_{22}\text{O}_3$ C: 74.42 H: 8.08	n_D^{25} 1.4960 74.84 8.15
214	285	$\text{CH}_3 > \text{CH} - \text{CH}_3$			a	$\text{C}_{23}\text{H}_{23}\text{O}_3\text{N}$ C: 76.01 H: 6.93 N: 3.85	n_D^{25} 1.5407 76.10 6.88 3.62
215	286	$\text{CH}_3 -$			a	$\text{C}_{19}\text{H}_{22}\text{O}_3$ C: 76.48 H: 7.43	$n_D^{25.5}$ 1.5202 76.41 7.55
216	287	$\text{C}_2\text{H}_5 -$			a	$\text{C}_{20}\text{H}_{24}\text{O}_3$ C: 76.89 H: 7.74	$n_D^{25.5}$ 1.5165 76.71 7.85
217	288	$\text{CH}_3 > \text{CH} - \text{CH}_3$			a	$\text{C}_{21}\text{H}_{25}\text{O}_3$ C: 77.27 H: 8.03	n_D^{25} 1.5153 77.25 8.09
218	289	$\text{C}_2\text{H}_5 -$			a	$\text{C}_{22}\text{H}_{26}\text{O}_3$ C: 77.27 H: 8.03	n_D^{27} 1.5150 77.45 8.01

PREPARATIVE TABLE

Preparation Exp. No.	Comp. No.	Z	Y	X	Esteri- fication Yield Method (%)	Physical Formula Calcd. (%)	Properties Refractive Index Found (%)
219	290	$\text{CH}_3 > \text{CH} - \text{CH}_3$			a	$\text{C}_{22}\text{H}_{20}\text{O}_3$ C: 77.61 H: 8.29	$n_D^{27} 1.5134$ $n_D^{27} 77.76$ 8.25
220	291	$\text{CH}_3 > \text{CH} - \text{CH}_3$			a	$\text{C}_{23}\text{H}_{20}\text{O}_3$ C: 78.37 H: 8.01	$n_D^{27} 1.5363$ $n_D^{27} 78.43$ 8.08
221	292	$\text{CH}_2=\text{CHCH}_2-$			a	$\text{C}_{23}\text{H}_{20}\text{O}_3$ C: 78.83 H: 7.48	$n_D^{25} 1.5345$ $n_D^{25} 78.85$ 7.48
222	293	$\text{CH}\equiv\text{CCH}_2-$			a	$\text{C}_{23}\text{H}_{24}\text{O}_3$ C: 79.28 H: 6.94	$n_D^{25} 1.5363$ $n_D^{25} 79.20$ 7.02
223	294	$\text{CH}_3 > \text{CH} - \text{CH}_3$			a	$\text{C}_{20}\text{H}_{26}\text{O}_3$ C: 76.40 H: 8.34	$n_D^{28} 1.4995$ $n_D^{28} 76.49$ 8.55
224	295	$\text{CH}_3 > \text{CH} - \text{CH}_2 -$			a	$\text{C}_{24}\text{H}_{26}\text{O}_3$ C: 79.53 H: 7.23	$n_D^{22} 1.5356$ $n_D^{22} 78.91$ 7.28

PREPARATIVE TABLE

Preparation Exp. No.	Comp. No.	Z	Y	X	Esteri- fication Method (%)	Physical Formula Calcd. (%)	Properties Refractive Index Found (%)
225	296	CH_3CH_2-			a	$\text{C}_{12}\text{H}_{14}\text{O}_2$ C: 82.46 H: 7.55	n_D^{20} 1.5238 82.41 7.53
226	297	CH_3CH_2-			a	$\text{C}_{19}\text{H}_{22}\text{O}_3$ C: 76.48 H: 7.43	n_D^{20} 1.5542 76.55 7.37
227	298	$\text{CH}_3 > \text{CH}-$ CH_3			a	$\text{C}_{23}\text{H}_{26}\text{O}_3\text{S}$ C: 73.86 H: 6.45 S: 7.89	n_D^{20} 1.5587 73.92 6.40 7.81
228	299	$\text{CH}_3 > \text{CH}-$ CH_3			a	$\text{C}_{23}\text{H}_{26}\text{O}_4$ C: 75.80 H: 6.64	n_D^{20} 1.5366 75.77 6.72
229	300	$\text{CH}_3 > \text{CH}-$ CH_3			a	$\text{C}_{23}\text{H}_{26}\text{O}_3$ C: 78.82 H: 7.48	n_D^{20} 1.5412 78.79 7.55 (

Preparation 1

Preparation of 5'-benzyl-3'-furylmethyl- α -ethyl phenylacetate (Compound No. 1)

6.20 g (0.02 mole) of α -ethylphenylacetic anhydride and 3.76 g (0.02 mole) of 5-benzyl-3-furylmethylalcohol were dissolved in 50 ml of dry pyridine and the mixture was stirred at room temperature for 2 hours. The resulting reaction mixture was poured into 100 g of ice water and extracted with three 20 ml portions of ethyl ether. The combined ether layer was then extracted with two 20 ml portions of 5% aqueous sodium hydroxide to remove α -ethylphenylacetic acid as a by-product. The ether layer was washed successively with 10% hydrochloric acid, saturated aqueous sodium bicarbonate and saturated sodium chloride, dried over anhydrous sodium sulfate, and the ether was removed under reduced pressure to obtain 6.25 g of crude ester as a pale yellow oily substance. The resulting oily substance was then purified by column chromatography using 120 g of activated alumina and a developing solvent of benzene-*n*-hexane (1:3) to obtain 5.68 g (85% theoretical yield) of the desired ester as a colorless oily substance.

n_D^{17} 1.5545

$\nu_{\max}^{\text{film}}$ 3005, 1724, 1550, 1407, 1180, 806 cm^{-1}

$\delta_{\text{ppm}}^{\text{CCl}_4}$ 7.16 (s, 5H), 7.15 (s, 5H), 7.2 (1H), 5.79 (bs, 1H), 4.78 (s, 2H), 3.78 (s, 2H), 3.31 (t, 1H, $J=7\text{Hz}$), 1.3—2.3 (m, 2H), 0.83 (t, 3H, $J=7\text{Hz}$)

Preparation 2.

*Preparation of *m*-phenoxybenzyl- α -ethylphenylacetate (Compound No. 2)*

2.00 g (0.01 mole) of *m*-phenoxybenzyl alcohol and 1.19 g (0.015 mole) of dry pyridine were dissolved in 20 ml of benzene, and 1.83 g (0.01 mole) of α -ethylphenylacetyl chloride dissolved in 5 ml of dry benzene was added dropwise thereto under ice-cooling. After completion of addition, the mixture was stirred at room temperature for 3 hours to complete the reaction, and the reaction mixture was poured into 30 g of ice-water. The mixture was separated, and the aqueous layer was extracted with two 10 ml portions of benzene. The combined benzene layer was washed successively with 5% hydrochloric acid, saturated aqueous sodium bicarbonate and saturated aqueous sodium chloride, and benzene was removed under reduced pressure. The resulting crude ester was charged onto a column packed with 40 g of activated alumina using a mixture of benzene-*n*-hexane (1:3) as an eluent to obtain 3.15 g (91% theoretical yield) of the purified ester.

n_D^{22} 1.5712

$\nu_{\max}^{\text{film}}$ 3030, 1740, 1590, 1470, 1260, 1220, 1160 cm^{-1}

$\delta_{\text{ppm}}^{\text{CCl}_4}$ 7.4—5.8 (m, 14H), 4.95 (s, 2H), 3.4 (t, 1H, $J=8\text{Hz}$), 2.3—1.1 (m, 2H), 0.85 (t, 3H, $J=8\text{Hz}$)

Preparation 17.

Preparation of 5'-benzyl-3'-furylmethyl- α -cyclohexylphenylacetate (Compound No. 17)

2.82 g (0.015 mole) of 5-benzyl-3-furylmethyl alcohol and 2.22 g (0.01 mole) of ethyl- α -cyclohexylphenylacetate were dissolved in 50 ml of dry toluene and 0.1 g of sodium hydride was added thereto as a catalyst. The mixture was charged into a Teflon Spinning Band rectification tower and ethanol formed as a by-product was removed while heating and stirring. The reaction was completed in about 1 hour, and the reaction mixture was allowed to stand and cooled to room temperature and poured into 30 g of ice-water. The layers were separated to remove the toluene layer and the toluene layer was washed with saturated aqueous sodium chloride. Toluene was removed under reduced pressure, and the resulting crude ester was subjected to a column packed with 50 g of activated alumina using benzene-*n*-hexane (1:3) as an eluent to obtain 2.79 g (72% theoretical yield) of the purified ester as white crystals. Melting point, 51—53°C.

$\nu_{\max}^{\text{nujol}}$ 3035, 1738, 1606, 1500, 1454, 1155 cm^{-1}

$\delta_{\text{ppm}}^{\text{CCl}_4}$ 7.3—6.9 (m. 11H), 5.80 (bs. 1H),
4.77 (AB. q 2H), 3.70 (S. 2H),
3.06 (d. 2H, $J=10\text{Hz}$), 2.1—0.6 (m 10H)

Preparation 5.

- 5 *Preparation of dimethylmaleimidomethyl- α -allylphenylacetate (Compound No. 5)* 5
1.74 g (0.01 mole) of N-chloromethyldimethylmaleimide and 2.93 g (0.01 mole) of silver α -allylphenylacetate were added to 25 ml of dimethylformamide and the mixture was allowed to stand overnight at room temperature. The precipitated crystals were filtered and dimethylformamide was distilled off under reduced pressure. The resulting crude ester was subjected to a silica gel column (90 g) using a mixture of chloroform-carbon tetrachloride (2:1) as an eluent to obtain 2.43 g (75% theoretical yield) of the desired ester as a white oily substance. 10

$n_D^{22.0}$ 1.5349

$\nu_{\text{max}}^{\text{film}}$ 1780, 1740, 1720, 1640, 1600, 1140, 910 cm^{-1}

- 15 $\delta_{\text{ppm}}^{\text{CDCl}_3}$ 7.15 (S. 5H), 6.0—4.9 (m. 3H), 3.48 (t. 3H, $J=10\text{Hz}$), 3.0—2.0 (m. 2H), 2.0 (S. 6H) 15

Preparation 22.

- 20 *Preparation of 5'-benzyl-3'-furylmethyl- α -isopropyl-4-methoxyphenylacetate (Compound No. 22)* 20
1.90 g (0.01 mole) of 5'-benzyl-3-furfuryl alcohol and 1.58 g (0.02 mole) of pyridine were dissolved in 50 ml of dry benzene, and 2.30 g (0.01 mole) of α -isopropyl-4-methoxyphenylacetyl chloride dissolved in 5 ml of dry benzene were added dropwise to the solution over about 30 minutes. After completion of the addition, the mixture was stirred at room temperature for 3 hours to complete the reaction. The reaction mixture was poured into 50 g of ice-water followed by separating the benzene layer, and the aqueous layer was extracted with two 20 ml portions of benzene. The combined benzene layer was washed successively with 5% hydrochloric acid, saturated aqueous sodium bicarbonate and saturated aqueous sodium chloride. A yellow oily substance obtained after removal of benzene was subjected to a column packed with 25 g of activated alumina using benzene-*n*-hexane (1:3) as an eluent to obtain 3.33 g (88.0% theoretical yield) of the purified ester as a colorless oily substance. 25 30

n_D^{17} 1.5470

- 35 $\nu_{\text{max}}^{\text{film}}$ 1735, 1617, 1515, 1250, 1032, 830, 730 cm^{-1} 35

$\delta_{\text{ppm}}^{\text{CCl}_4}$ 0.65 (d. 3H, $J=7\text{Hz}$), 0.95 (d. 3H, $J=7\text{Hz}$),
1.7—2.5 (m. 1H), 2.97 (d. 1H, $J=11\text{Hz}$),
3.67 (S. 3H), 3.81 (S. 2H), 4.78 (d.d. 2H),
5.83 (b.S. 1H), 6.90 (d.d. 4H), 7.1—7.3 (m. 6H)

Preparation 27.

- 40 *Preparation of 3,4,5,6-tetrahydrophthalimidomethyl- α -ethyl-2,4,6-trimethylphenylacetate (Compound No. 27)* 40
10.31 g (0.05 mole) of α -ethyl-2,4,6-trimethylphenylacetic acid and 9.05 g (0.05 mole) of 3,4,5,6-tetrahydrophthalimidomethylol were dissolved in 100 ml of dry benzene, and 16.51 g (0.08 mole) of dicyclohexylcarbodiimide was added to the solution. The mixture was then allowed to stand overnight in a sealed vessel. Next day, the mixture was heated at reflux to complete the reaction, and, after allowing to cool, the precipitated dicyclohexylurea was separated by filtration. A viscous oily substance obtained by concentration of the filtrate was subjected to a silica gel column (360 g) to obtain 11.3 g (61.18% theoretical yield) of the purified ester as a colorless viscous oily substance. 45 50

n_D^{25} 1.5399

$\nu_{\text{max}}^{\text{film}}$ 1780, 1740, 1720, 1511, 1405, 1140 cm^{-1}

$\delta_{\text{ppm}}^{\text{CCl}_4}$ 0.85 (t. 3H, J=7Hz), 1.5—2.3 (m. 2H),
2.3 (b.s. 9H), 3.32 (t. 3H, J=8Hz),
1.5—2.0 (m. 4H), 2.0—2.5 (m. 4H),
5.34 (d.d. 2H), 7.0—7.3 (m. 2H)

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Preparation 47.

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Preparation of 2'-allyl-3'-methyl-2'-cyclopentene-1'-one-4'-yl- α -ethyl-3-methoxyphenylacetate (Compound No. 93)

7.41 g (0.02 mole) of α -ethyl-3-methoxyphenylacetic anhydride and 1.52 g (0.01 mole) of 2-allyl-3-methyl-4-hydroxy-2-cyclopentene-1-one were dissolved in 50 ml of dry pyridine, and the mixture was stirred overnight at room temperature. On next day, the reaction mixture was poured into 100 g of ice-water and extracted with three 20 ml portions of ethyl ether. The combined ether layer was then extracted with two 30 ml portions of 5% aqueous sodium hydroxide to remove a carboxylic acid formed as a by-product. The ether layer was washed successively with 10% aqueous hydrochloric acid, saturated aqueous sodium bicarbonate and saturated aqueous sodium chloride and dried over anhydrous sodium sulfate. Removal of ether under reduced pressure yielded 3.2 g of a crude ester. The product was then subjected to a column packed with 20 g of activated alumina using benzene-*n*-hexane (1:3) as an eluent to obtain 2.73 g (83.1% theoretical yield) of the desired ester.

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n_D^{19} 1.5211

$\nu_{\text{max}}^{\text{film}}$ 1730, 1710, 1150, 1140, 1000, 910 cm^{-1}

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$\delta_{\text{ppm}}^{\text{CCl}_4}$ 0.90 (t. 3H, J=8Hz), 1.5—3.0 (m. 11H),
3.36 (t. 1H, J=9Hz), 3.67 (s. 1H),
4.7—6.0 (m. 3H), 6.5—6.9 (m. 4H)

Preparation 46.

Preparation of 3'-phenoxybenzyl- α -isopropyl-3-methoxyphenylacetate (Compound No. 87)

8.01 g (0.04 mole) of *m*-phenoxybenzyl alcohol and 7.09 g (0.03 mole) of ethyl α -isopropyl-3-methoxyphenylacetate were dissolved in 100 ml of dry toluene, and 0.1 g of sodium hydride was added thereto as a catalyst. The mixture was then charged in a Teflon Spinning Band rectifier tower having a length of 50 cm and heated while stirring. The reaction was completed in about 3 hours by removing ethanol as an azeotropic distillation with toluene at the top of the tower. After allowing to stand and cooling the mixture was poured into cold water to separate layers. Removal of toluene by distillation under reduced pressure yielded 11.5 g of a crude ester. The product was then subjected to a column packed with 55 g of activated alumina using benzene-*n*-hexane (1:3) as an eluent to obtain 10.12 g (86.4% theoretical yield based on the starting ethyl ester) of the desired ester.

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n_D^{17} 1.5377

$\nu_{\text{max}}^{\text{film}}$ 3060, 1738, 1590, 1490, 1255, 1145, 775, 690 cm^{-1}

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$\delta_{\text{ppm}}^{\text{CCl}_4}$ 0.70 (d. 3H, J=7Hz), 0.97 (d. 3H, J=7Hz),
0.9—2.6 (m. 1H), 3.08 (d. 1H, J=11Hz),
3.65 (s. 3H), 4.95 (AB Type d.d. 2H),
6.5—7.4 (m. 13H)

Preparation 48.

Preparation of 3'-phenoxybenzyl-2-(1',2',3',4'-tetrahydronaphthalene-8'-yl) isovalerate (Compound No. 43)

3.95 g (0.015 mole) of *m*-phenoxybenzyl bromide, 2.32 g (0.01 mole) of 2-(1',2',3',4'-tetrahydronaphthalene-8'-yl) isovaleric acid and 2.02 g (0.02 mole) of triethylamine were added to 50 ml of dimethylformamide and the mixture was stirred overnight at room temperature. The reaction mixture was poured into 50 g of ice-water and extracted with three 30 ml portions of ethyl ether. The combined ether layer was washed successively with 5% hydrochloric acid, saturated aqueous sodium bi-carbonate and saturated aqueous sodium chloride and dried over anhydrous sodium sulfate. Removal of ethyl ether by distillation under reduced

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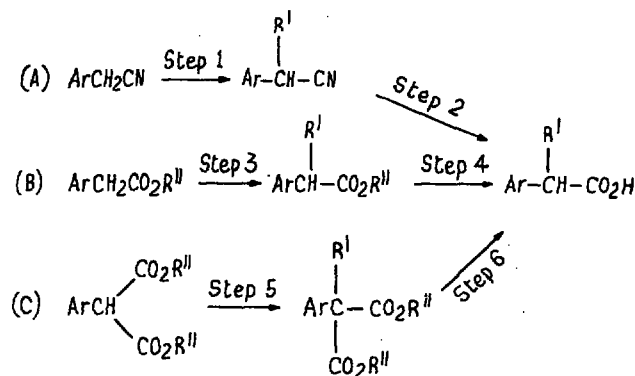
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pressure yielded a crude ester which was then subjected to a column packed with 20 g of activated alumina using benzene-n-hexane (1:3) as an eluent to obtain 3.45 g (83.2% theoretical yield based on the carboxylic acid starting material) of the desired ester as a colorless oily substance.

5	n_D^{19}	1.5660	5
	$\nu_{\max}^{\text{film}}$	3060, 1736, 1588, 1490, 1255, 770, 690 cm^{-1}	
	$\delta_{\text{ppm}}^{\text{CCl}_4}$	0.68 (d. 3H, $J=7\text{Hz}$), 1.03 (d. 3H, $J=7\text{Hz}$), 1.5—2.0 (m. 4H), 2.1—2.6 (m. 1H), 2.5—3.0 (m. 4H), 2.48 (d. 1H, $J=11\text{Hz}$), 4.74 (s. 2H), 6.6—7.4 (m. 12H)	
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Most of the important intermediates of the present invention, i.e., disubstituted acetic acid, can effectively be prepared in high yields via one of the alternative procedures (A), (B) and (C) given below.



wherein Ar represents an aryl group, R' represents an alkyl, alkenyl or alkynyl group, R'' represents hydrogen or a lower alkyl group, and R''' represents a lower alkyl group.

Step 1: This reaction can be accomplished by alkylating the corresponding arylacetonitrile with an appropriate halide or sulfoxylate of the formula R'—X in an inert solvent (for example, an ether, tetrahydrofuran, benzene or toluene and including liquid ammonia when NaNH₂ and the like is used as a base described below) in the presence of a base such as an alkali metal, alkali metal hydride, alkali metal amide or the like at room temperature or an elevated temperature.

Step 2: This reaction can be accomplished under the well-known conditions commonly used for hydrolysis of a nitrile group, i.e., by heating the nitrile with a mineral acid or an alkali metal hydroxide.

Steps 3 and 4: These reactions can be accomplished by alkylating the corresponding phenylacetic acid or a lower-alkyl ester thereof with an appropriate halide or sulfoxylate of the formula R'—X in an inert solvent in the presence of a base such as an alkali metal hydroxide or a hydride thereof, *n*-butyl lithium and the like at room temperature or an elevated temperature, and when the lower-alkyl ester is used for the alkylation, hydrolyzing the resulting ester with an appropriate acid or alkali in the usual manner.

Step 5: This reaction can be accomplished by reacting an arylmalonic acid ester (which is easily obtainable by carbalkoxylation of the corresponding arylacetic ester) with an appropriate halide or sulfoxylate of the formula R'—X in the presence of an alkali metal alkoxide or an alkali metal hydride as a base in an inert solvent or an alcohol corresponding to the alkali metal alkoxide.

Step 6: This reaction can be accomplished under the well-known conditions commonly used for hydrolysis of an ester, i.e., by hydrolyzing the ester with an acid or alkali to obtain the corresponding dicarboxylic acid followed by heat-decarbonization to obtain the desired carboxylic acid, or can be accomplished by heating the diester with an alkali metal alkoxide in an alcohol whereby the diester is easily converted into a monoester by decarboxylation and hydrolyzing the monoester by a well-known procedure to obtain the corresponding carboxylic acid in high yields.

The preparation of the intermediate carboxylic acids is illustrated in our co-pending application No. 13563/75 (Serial No. 1,439,616).

Although a compound which bears an isopropenyl group on α -position such as Compounds No. 83, No. 85, No. 125, can be prepared by the usual esterification method using corresponding acid chloride, the double bond of the isopropenyl group readily isomerizes to the α - β position to make the acid or acid chloride into a mixture of isomers in which the double bond is at different positions. A low yield was attained after chromatographic purification. Accordingly the following route (A) seems to be better than the conventional methods (B1 to 3) for the preparation of such compounds.

(A) *3'-Phenoxybenzyl- α -isopropenyl-4-methoxyphenyl-acetate* (Compound No. 82)

(1) To a solution of isopropylmagnesium bromide, which was prepared from 38.1 g of isopropylbromide and 7.3 g of magnesium in 90 ml of dry ether, was added a solution of 4-methoxyphenylacetic acid (16.6 g) in 100 ml of dry tetrahydrofuran at an ice-bath temperature; thereafter the solution was stirred at room temperature for 2 hours. Dry acetone (7.0 g), diluted with 20 ml of dry toluene, was added to the solution, and it was heated to reflux for 5 hours. The cooled solution was acidified with 15% sulfuric acid; the aqueous phase was then separated, and extracted with ether. The combined organic layers were extracted with 10% sodium carbonate solution. The carbonate extract was acidified with concentrated hydrochloric acid and extracted with ether. The ether extract was dried over anhydrous sodium sulfate. Removal of the solvent and a recrystallization from ethyl acetate afforded 12.4 g of 4-methoxy- β , β -dimethylatropic acid (55.2%, m.p. 124—125°C).

(2) To a solution of 4-methoxy- β , β -dimethylatropic acid (5.0 g) and triethylamine (4.5 g) in 50 ml of dimethylformamide, were added 7.0 g of 3-phenoxybenzylbromide gradually at an ice-bath temperature, and stirred overnight at room temperature. The mixture was poured into cold 10% H_2SO_4 and extracted with ether. The ether layer was washed with 10% sodium carbonate solution and dried over anhydrous sodium sulfate. Removal of the solvent gave 4.8 g of crude hydroxyester, which was dehydrated with P_2O_5 in benzene at 80°C for 13 hours. Filtration, and removal of the solvent gave crude isopropenylester as a dark oil. Purification with silica-gel chromatography afforded 1.9 g of pure ester. (40.5%, n_D^{16} 1.5798).

(B) (1) *Ethyl-2-(cyclohexane-1'-ol-1'-yl)-butyrate*

This was prepared from ethyl-2-bromobutyrate (29.3 g), cyclohexanone (14.7 g) and zinc (9.51 g) in benzene (50 ml) and toluene (25 ml) under usual Reformatsky conditions (b.p. 116—117°/4 mmHg, yield 16.4 g, 51.0%).

(2) *Ethyl-2(cyclohexene-1-yl)-butyrate*

The above hydroxyester (16.4 g) was heated under reflux with phosphorus pentoxide (11 g) in 60 ml of dry benzene for 3 hours. The cooled mixture was poured onto 80 ml of cold water, the organic layer was separated and washed with saturated sodium chloride solution. Solvent was removed *in vacuo*, and the residue was distilled under reduced pressure to afford 11.6 g of pale yellow oil. (76.5% b.p. 88—92°/4 mmHg).

(3) *Ethyl-2,3-diethyl-3-hydroxy-pentanoate*

In a similar manner to (1) above, this was prepared from 3-pentanone and ethyl-2-bromobutyrate. (Yield 52.8%, b.p. 113—121°/20 mmHg).

The hydroxyester obtained was dehydrolyzed with phosphorus pentoxide in benzene in the manner described above. (Yield 68.2%, b.p. 95—98°/22 mmHg).

The compounds of the type exemplified by Compound Nos. 18, 21, 245, 246 and 248 were prepared from the corresponding carboxylic acid or an acid chloride derived therefrom which was obtained by hydrolyzing the ethyl ester prepared in a similar manner to that described in (B) (1), (2) and (3) above. The hydrolysis can be effected by the conventional procedure using sodium hydroxide or potassium

hydroxide in methanol at room temperature. The carboxylic acid thus obtained was found to contain a small amount of isomers with respect to the double bonds (up to about 10%), but the crude carboxylic acid was subjected to esterification without isolating impurities (isomers) and the product was purified by silica gel chromatography in the final step.

The substituted ester compounds represented by the general formula (I) exhibit excellent pesticidal activity and repellent activity against mites, as well as exhibiting a synergistic activity with other biologically active agents. They may be employed at low cost as pesticidal compositions for use in a wide variety of applications in agriculture, horticulture, forestry, and sanitation, as well as in cereal stockrooms and in compositions for controlling mites.

In the practical use of these compounds, an appropriate amount of one or more of solvents, fillers, diluents, active agents, dispersion agents, surface active agents, spreaders, pressure-imparting agents, emulsifying agents and attractants may be added to the ester compounds of the formula (I) to form an emulsifiable concentrate, a wettable powder, a dust, granules, fine grains, a coating agent, a powder, an oil preparation, an aerosol, a mosquito coil, a smoking agent, a fumigating agent, or a mosquito incense agent for electrical vaporization.

The effect of the pesticidal compositions of this invention will now be illustrated by the following Experimental Examples.

EXPERIMENTAL EXAMPLE 1.

An emulsifiable concentrate was prepared by blending each of the Compounds Nos. 1 to 300 of the present invention, xylol and Sorpol SM-200 (trade name; manufactured by Toho Chemical Co., Ltd.) in proportions of 25%, 50% and 25% (by weight), respectively. 20 to 25 day-old rice plants were grown in pots after seeding and were sprayed with a 300-fold dilute solution of a different one of the emulsifiable concentrate thus prepared. A 300-fold dilute solution of a commercial agent, being carbaryl 30% wettable powder diluted with water was used as a control. In each case an amount of 10 ml/pot was applied and then the pots were covered by a cylindrical metal net. 15 smaller brown planthoppers (*Delphacodes striatella* Fallén) were released into each of the pots treated with the carbaryl wettable powder, and Compounds Nos. 1 to 21 and 102 to 110, while 15 green rice leafhoppers (*Nephotettix bipunctatus cincticeps* Uhler) were released in each of the pots treated with the carbaryl wettable powder and Compounds Nos. 22 to 101 and 111 to 300. Observation on survival one day after the treatment revealed that each of the compounds of this invention exhibited more than 90% killing effect than carbaryl.

EXPERIMENTAL EXAMPLE 2.

Of the emulsifiable concentrates prepared in Experimental Example 1, each of those prepared from the Compounds listed in Table 1 below was diluted with water to each of test concentrations there shown and a 200 ml portion thereof was added to a 300 ml volume beaker. 30 larvae of mosquito per group were released into each of the beakers and allowed to stand for 1 day. Survival was observed and a LC_{50} (50% lethal concentration) was determined by calculating the percentage killing in each case. The results obtained are also shown in Table 1. As a control lindane emulsifiable concentrate was used.

TABLE I
Insecticidal Activity on Larvae of Mosquito (*Culex pipiens*)

Test emulsifiable concentrate	LC ₅₀ (ppm)	Test emulsifiable concentrate	LC ₅₀ (ppm)
Compound No. 1	0.0015	Compound No. 2	0.0034
„ 10	0.0030	„ 14	0.0026
„ 16	0.0014	„ 102	0.0095
„ 103	0.0092	„ 104	0.0120
„ 105	0.0105	„ 110	0.0125
„ 111	0.0025	„ 112	0.0046
„ 113	0.0053	„ 115	0.0050
„ 119	0.0044	„ 120	0.0040
„ 121	0.0037	„ 125	0.0032
„ 126	0.0056	„ 128	0.0047
„ 145	0.0039	„ 165	0.0012
„ 167	0.0043	„ 177	0.0074
„ 180	0.0072	„ 181	0.00820
„ 183	0.0885	„ 184	0.0078
„ 204	0.0075	„ 206	0.0032
„ 210	0.0035	„ 212	0.0037
„ 214	0.0127	„ 215	0.0132
„ 226	0.0135	„ 227	0.0019
„ 231	0.0014	„ 298	0.0097
Lindane	0.22		

EXPERIMENTAL EXAMPLE 3.

A 2000-fold dilute solution of each of the emulsifiable concentrates prepared in Experimental Example 1 from the compounds shown in Table 2 below was sprayed after seeding in an amount of 10 ml/pot on a different 12 day-old mottled kidney bean seedling grown in a pot. The seedling thus treated was cut off and put in a wide-mouthed bottle. In the same manner, an untreated mottled kidney bean seedling in the same stage was cut off and put in another wide-mouthed bottle. Another fresh seedling was fixed with pins bridging on the former treated seedling and the latter untreated seedling. A leaf of mottled kidney bean on which a number of spider mites (*Tetranychus telarius*) were parasitic was placed on the middle of the bridging seedling and allowed to stand for 2 days. Activity on repellancy was assessed by investigating the numbers of mites swarming on the treated seedling and the untreated seedling. The assessment standards were as follows:

		Assessment	
15	—: The ratio of the number of mites on the untreated seedling to that on the treated seedling	1:1	15
		up to 4:1 +	
		greater than 4:1 ++	

The results obtained are shown in Table 2 below.

TABLE 2.
Repellent Activity on Spider Mites

Test emulsifiable concentrate	Repellency	Test emulsifiable concentrate	Repellency
Compound No. 1	++	Compound No. 3	+
„ 4	++	„ 10	++
„ 18	+	„ 23	+
„ 29	++	„ 35	+
„ 45	++	„ 65	+
„ 73	+	„ 82	++
„ 92	++	„ 98	++
„ 116	++	„ 117	++
„ 118	++	„ 121	++
„ 124	+	„ 127	++
„ 130	+	„ 165	++
„ 168	++	„ 175	++
„ 176	++	„ 177	++
„ 178	++	„ 200	++
„ 204	++	„ 206	++
„ 210	++	„ 216	++
„ 217	++	„ 218	++
„ 219	++	„ 220	++
„ 221	++	„ 227	++
„ 234	++	„ 235	++

EXPERIMENTAL EXAMPLE 4.

0.2% oil preparation was prepared from each of the Compounds Nos. 1, 2, 8, 14, 22, 25, 26, 27, 51, 62, 73, 82, 86, 88 to 90, 92, 94, 96, 111, 119, 121, 165, 175, 180, 184, 185, 195, 200, 201 and 208 and further allethrin as a control using deodorized kerosene. About 50 adult mosquitoes (*Culex pipens*) were released in a glass box, (70 Cm)³, and sprayed with each of the oil preparations obtained above in an amount of 0.7 ml under a pressure of 1.5 Kg/cm². It was found that more than 80% of the mosquitoes were knocked down by both allethrin and the compounds of this invention.

EXPERIMENTAL EXAMPLE 5.

20 oriental house flies per group were released in a glass box, (70 cm)³, and sprayed with each of the oil preparations prepared in Experimental Example 4 from the Compounds shown in Table 3 below and allethrin in an amount of 0.7 ml under a pressure of 1.5 Kg/cm². The test was repeated several times and the knock-

down of the flies was observed to determine KT_{50} (50% knock-down time). The results obtained are shown in Table 3.

TABLE 3.
Activity on Knock-Down Against Oriental House Flies

Test oil preparation	KT_{50} (sec.)	Test oil preparation	KT_{50} (sec.)
Compound No. 1	167	Compound No. 8	128
„ 22	136	„ 51	104
„ 62	154	„ 63	140
„ 82	132	„ 88	147
„ 89	155	„ 96	92
„ 111	138	„ 119	132
„ 121	130	„ 165	145
„ 175	152	„ 180	157
„ 184	142	„ 185	137
„ 195	140	„ 200	114
„ 201	105	„ 208	150
Allethrin	186		

EXPERIMENTAL EXAMPLE 6.

5 To each of the Compounds Nos. 22, 51, 62, 63, 82, 86, 125, 150, 160, 176, 177, 178, 184, 185, 191, 195, 200, 201, 204, 208, 210, 212 and 226 was added piperonyl butoxide in an amount of 5 times that of the active ingredient to prepare an acetone solution having a given concentration. Each of the thus prepared acetone solutions was applied onto a thoracic dosal plate for oriental house flies using a microsyringe to observe the synergistic effect of piperonyl butoxide on insecticidal activity. Potentiation magnification of insecticidal activity by the addition of piperonyl butoxide is shown in Table 4.

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TABLE 4.
Potential Effect on Insecticidal Activity by the Addition of Piperonyl Butoxide

Test compound	Potential magnification	Test compound	Potential magnification
Compound No. 22	5.0	Compound No. 51	7.2
" 62	5.3	" 63	4.8
" 82	6.7	" 86	4.5
" 119	5.5	" 125	6.0
" 150	4.2	" 160	7.2
" 176	5.2	" 177	5.8
" 178	5.4	" 184	5.6
" 185	5.0	" 191	4.3
" 195	5.7	" 200	7.5
" 201	7.0	" 204	4.7
" 206	5.1	" 208	5.2
" 210	4.8	" 212	5.0
" 226	4.5		

As is apparent from the above Experimental Examples, the compounds of this invention exhibit an excellent biological activity on various noxious insects and mites and are also of low toxicity.

Oral toxicity to mice for representative compounds is shown in Table 5 below.

TABLE 5.

Test compound	LD ₅₀ (mg/Kg)	Test compound	LD ₅₀ (mg/kg)
Compound No. 1	>1000	Compound No. 2	>1000
" 8	750	" 22	900
" 62	>1000	" 63	>1000
" 80	>1000	" 82	>1000
" 108	>1000	" 119	>1000
" 125	>1000	" 129	>1000
" 130	>1000	" 145	>1000
" 150	>1000	" 176	>1000
" 184	940	" 206	>1000

The compositions according to the present invention are very useful for controlling insanitary insects such as mosquitoes, flies and cockroaches, grain

- insects such as rice weevil (*Calandra oryzae*) and mites, as well as agricultural noxious insects such as plant-hoppers, green rice leafhopper (*Nephotettix bipunctatus cincticeps* Uhler), cabbage army worms (*Barathra brassicae* Linne), diamond-back moths (*Plutella maculipennis* Curtis), noctuidae, cabbage worm (*Pieris rapae* Linne), rice stem borer (*Chilo suppressalis* Walker), aphids, tortrixes and leaf-miners. 5
- They are also superior whenever they may be freely used for harvested crops, horticultural application, crops in a green house, and packaging materials for foodstuffs.
- 10 In preparing the compositions according to the present invention, it is possible to obtain more better control effects by employing a combination of two or more compounds of the general formula (I), and furthermore, it is possible to obtain various compositions which are useful for a wide variety of applications, by combining one or more compounds of the formula (I) with other pesticidal compounds, for example, organochlorine compounds such as DDT, BHC or 15 Methoxychlor; organic phosphorus compounds such as Sumithion (trade name of Sumitomo Chemical Company Limited), DDVP, diazinon, phenthion and Cyanox (trade name of Sumitomo Chemical Company Limited); carbamates such as 1-naphthyl-N-methylcarbamate, 3,4-dimethylphenyl N-methylcarbamate and 3,5-dimethylphenyl N-methylcarbamate; cyclopropanecarboxylic acid esters such as 20 pyrethrin, allethrin, Neopynamin (trade name of Sumitomo Chemical Company Limited), Chrysron (trade name of Sumitomo Chemical Company Limited), 3-phenoxybenzyl chrysanthemate, 5-propargylfurfuryl chrysanthemate and their geometrical or optical isomers; piperonyl butoxide, sulfoxide, safroxane, isobornyl thiocyno acetate (I.B.T.A.) and octachloro dipropyl ether (S-421) which 25 potentiate the effect of the esters synergistically; terephthalic acid, isophthalic acid and BHT which are generally used in fumigating preparations; phenol derivatives used as stabilizers; bisphenol derivatives; arylamines such as phenyl- α -naphthylamine, phenyl- β -naphthylamine, and a condensate of phenetidin and acetone; other insecticidal agents or miticidal agents such as Padan, Galecron; 30 antimicrobial agents; nematocidal agents; herbicidal agents; fertilizers and other agricultural agents. These compositions are expected to be useful for saving manpower in application of these agricultural agents and for obtaining synergistic activity between the active ingredients of the composition.
- 35 The preparation of compositions and the effect of compounds of this invention are further illustrated by the following Formulation and Application Examples. The parts used in Formulation Examples are by weight unless otherwise indicated.
- 40 **Formulation Example 1.**
To 20 parts of each of Compounds Nos. 1 to 110, there were added 10 parts of Sumithion (as described previously), 10 parts of Sorpol SM-200 (as described previously), 60 parts of xylol, and the mixture was thoroughly stirred and mixed to obtain an emulsifiable concentrate in each case. 40
- 45 **Formulation Example 2.**
To 10 parts of each of Compounds Nos. 111 to 192, there were added 10 parts of Cyanox (as described previously), 10 parts of Sorpol SM-200 (as described previously) and 70 parts of xylol, and the mixture was thoroughly stirred and mixed to obtain an emulsifiable concentrate in each case. 45
- 50 **Formulation Example 3.**
To 15 parts of each of Compounds Nos. 193 to 232, there were added 30 parts of piperonyl butoxide, 15 parts of Sorpol SM-200 (as defined previously) and 40 parts of xylol, and the mixture was thoroughly stirred and mixed to obtain an emulsifiable concentrate in each case. 50
- 55 **Formulation Example 4.**
To 15 parts of each of Compounds Nos. 233 to 300, there were added 20 parts of a 25% pyrethrin extract, 20 parts of piperonyl butoxide, 15 parts of Sorpol SM-200 (as described previously) and 30 parts of xylol, and the mixture was thoroughly stirred and mixed to obtain an emulsifiable concentrate in each case. 55
- 60 **Formulation Example 5.**
0.5 part of each of Compounds Nos. 1, 10, 102, 103, 108 and 111 to 115 was 60

dissolved in kerosene in an amount sufficient to make 100 parts thereby obtaining an oil preparation in each case.

Formulation Example 6.

To 0.2 part of each of Compounds Nos. 116 to 192, there were added 0.1 part of allethrin α -trans chrysanthemate and 1.5 parts of safroxane, and the mixture was dissolved in kerosene to prepare 100 parts of an oil preparation in each case.

Formulation Example 7.

To 0.2 part of each of Compounds Nos. 193 to 300, there were added 0.1 part of Neopynamine and 1.5 parts of S-421, and the mixture was dissolved in kerosene to prepare 100 parts of an oil preparation in each case.

Formulation Example 8.

To 10 parts of each of Compounds Nos. 1 to 110, there were added 10 parts of 1-naphthyl-N-methylcarbamate and 5 parts of Sorpol SM-200 (as described previously), followed by mixing. 75 parts of 300-mesh talc were then added to the mixture and the resulting blend was thoroughly stirred in a triturator to obtain a wettable powder in each case.

Formulation Example 9.

The active pesticidal ingredients shown as Compounds Nos. 1 to 10 in Table 6 below were respectively dissolved in 20 ml of methanol and the resulting solution was mixed with 100 g of a carrier for mosquito coils (a mixture of tabu powder, pyrethrum marc and wood powder in a proportion of 3:5:1, respectively), followed by blending uniformly. After the methanol had evaporated, 150 ml of water were added to the blend, and the mixture was thoroughly kneaded, molded and dried to prepare a mosquito coil in each case.

TABLE 6.
Formulations for Mosquito Coils

Composition No.		
1.	Compound No. 1 Allethrin	0.3 g 0.3 g
2.	Compound No. 8 Allethrin	0.3 g 0.3 g
3.	Compound No. 22 Allethrin BHT	0.3 g 0.2 g 0.3 g
4.	Compound No. 37 Allethrin	0.3 g 0.3 g
5.	Compound No. 51 Allethrin α -trans chrysanthemate BHT	0.3 g 0.1 g 0.4 g
6.	Compound No. 62 5-Propargylfurfuryl chrysanthemate BHT	0.2 g 0.2 g 0.8 g
7.	Compound No. 82 5-Propargyl-2-methyl-3-furylmethyl chrysanthemate BHT	0.3 g 0.1 g 0.4 g
8.	Compound No. 146 Allethrin d-cis, trans chrysanthemate BHT	0.3 g 0.1 g 0.5 g
9.	Compound No. 169 Allethrin BHT	0.3 g 0.2 g 0.5 g
10.	Compound No. 184 Allethrin BHT	0.3 g 0.3 g 0.3 g

Formulation Example 10.

The active pesticidal ingredients having one of the compositions shown in Table 7 below were respectively dissolved in a mixed solvent comprising xylol and refined kerosene (1:1 by volume) to prepare 15 parts of solution and the solution was charged into an aerosol dispensing container. After a valve was mounted on each container, the aerosol dispenser was pressurized by charging 85 parts of a propellant (for example, freon, vinyl chloride monomer or liquefied petroleum gas).

TABLE 7.
Aerosol Formulations

Composition No.		
1.	Compound No. 22 3-Phenoxybenzyl-d-cis, trans chrysanthemate	0.3 parts 0.1
2.	Compound No. 22 Neopynamin I.B.T.A.	0.2 0.2 1
3.	Compound No. 62 Allethrin α -trans chrysanthemate Safroxane	0.2 0.2 2
4.	Compound No. 62 DDVP	0.3 0.3
5.	Compound No. 82 Sumithion Neopynamin	0.2 0.3 0.2
6.	Compound No. 82 Piperonyl butoxide	0.4 2.0
7.	Compound No. 88 Neopynamin Chrysron	0.2 0.2 0.1
8.	Compound No. 89 Allethrin α -trans chrysanthemate	0.3 0.2
9.	Compound No. 96 Allethrin d-cis, trans chrysanthemate Safroxane	0.2 0.2 2
10.	Compound No. 102 Neopynamin Piperonyl butoxide	0.4 0.1 1.5
11.	Compound No. 103 Allethrin S-421	0.4 0.1 1.5
12.	Compound No. 108 25% Pyrethrin extract Piperonyl butoxide	0.4 0.5 1.0
13.	Compound No. 125 I.B.T.A.	0.4 2

Formulation Example 11.

The active pesticidal ingredients having one of the compositions shown in Table 8 below were respectively dissolved in an appropriate amount of chloroform, and the solution was adsorbed uniformly on the surface of asbestos having a size of 2.5 cm $\times$ 1.5 cm and a thickness of 0.3 mm. Another piece of asbestos having the same size and thickness was then placed on the treated surface of the above piece of asbestos to prepare a fibrous fumigatory pesticidal mat for heating on a hot plate. As a fibrous carrier, a material having the same characteristics as that of asbestos, such as a pulp board may also be used in place of asbestos.

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TABLE 8.
Formulation of Compounds for Impregnating Mats for Heating on a Hot Plate

Composition No.		
1.	Compound No. 51	0.05 g
	Allethrin	0.02 g
	Piperonyl butoxide	0.07 g
2.	Compound No. 63	0.07 g
	Allethrin α -trans chrysanthemate	0.01 g
	Piperonyl butoxide	0.1 g
3.	Compound No. 80	0.5 g
	5-Propargyl furylmethyl chrysanthemate	0.02 g
	Piperonyl butoxide	0.15 g
	BHT	0.1 g
4.	Compound No. 82	0.04 g
	Allethrin	0.04 g
	Piperonyl butoxide	0.08 g
	BHT	0.1 g
5.	Compound No. 88	0.05 g
	5-Propargyl-2-methyl-3-furylmethyl chrysanthemate	0.02 g
	Piperonyl butoxide	0.15 g
6.	Compound No. 103	0.05 g
	Allethrin	0.02 g
	Piperonyl butoxide	0.15 g
7.	Compound No. 107	0.05 g
	5-Phenoxybenzyl chrysanthemate	0.03 g
8.	Compound No. 125	0.05 g
	Allethrin	0.01 g

Formulation Example 12.

5 To 1 part of each of Compounds Nos. 22, 51, 62, 63, 83, 86, 94, 103, 108 and 125 were added 5 parts of piperonyl butoxide and the mixture was dissolved in 20 parts of acetone. After 94 parts of 300-mesh diatomaceous earth had been added, the resulting blend was thoroughly stirred and mixed in a triturator, and acetone was removed by evaporation to obtain a powder in each case. 5

Application Example 1.

10 10 third inster larvae of tobacco cutworm (*Spodoptera lituna* Fabricius) were placed in a glass tray having a high side-wall and a diameter of 14 cm, and 1 ml of a 200-fold dilute solution of each of the emulsifiable concentrates obtained in Formulation Examples 1 and 3 diluted with water was sprayed on the larvae by a sprayer, and the larvae thus treated were then transferred into a glass tray containing feeds and allowed to stand. Two days after the treatment, more than 80% of the larvae were found to be killed in each case. 15

Application Example 2.

20 An area of a radish field in a 5—6 leaf stage, a number of green peach aphids (*Myzus persicae* Sulza) was sprayed at a rate of 424 l/acre with an atomized 200-fold dilute solution of each of the emulsifiable concentrates obtained in Formulation Examples 1, 2 and 4 diluted with water. Investigation two days after treatment revealed that the density of aphids was reduced to less than 1/10 the density before treatment in each case. 20

Application Example 3.

25 A piece of plywood board (15 cm x 15 cm) was treated with a 200-fold dilute solution of each of the emulsifiable concentrates obtained in Formulation 25

Examples 1 and 2 diluted with water in an amount of 50 ml/m², followed by drying. Adult German cockroaches (*Blattella germanica* Linne) were then brought into contact with the plywood board thus treated for 1 hour, and it was found that more than 80% of the cockroaches were killed three days after contact with the board.

5 Application Example 4.

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10 A field of ripe egg-plants harbouring a number of larvae of potato lady beetle (*Epilachna sparsa orientalis* Dieke) was sprayed in an amount of 424 l/acre) with an atomized 200-fold dilute solution of each of the emulsifiable concentrates obtained in Formulation Example 1. Investigation on knock-down thirty minutes after the treatment revealed that 90% of the larvae had fallen to the ground. A further investigation on density of larvae 24 hours after the treatment revealed that almost 100% of the larvae had been controlled as compared with the density of the larvae before treatment.

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15 Application Example 5.

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20 45 day-old rice plants were grown after seeding in Wagner pots (1/50000) and respectively sprayed with a 400-fold dilute solution of each of the wettable powders obtained in Formulation Example 8 in an amount of 10 ml/pot. the pots were then covered with a cylindrical metal net and about 20 larvae of leaf hopper (*Cicadula sexnotata*) were released therein. In each case, more than 80% of the larvae were found to be killed one day after the release.

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Application Example 6.

25 Each of the dusts obtained in Formulation Example 12 was placed uniformly at the bottom of a glass tray having a diameter of 14 cm and a high side-wall in an amount of 2 g/m² and butter was applied to the glass wall except for about 1 cm portion of the bottom. 10 adult German Cockroaches per group were then released in the glass trays and, after contact for 30 minutes, the larvae were transferred to a fresh glass container. In each case, more than 80% of the larvae were found to be killed three days after the treatment.

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Application Example 7.

30 Each of the oil preparations obtained in Formulation Example 5 was atomized using Campel's turn-table apparatus [Soap and Sanitary Chemicals, 14, No. 6, 119 (1938)] in an amount of 5 ml. 20 seconds after atomizing, the shutter was opened and 100 adult oriental house flies (*Musca domestica vicina* Maquant) per group were exposed to the falling atomized fumes for a period of 10 minutes. The flies thus treated were then fed and allowed to stand. More than 80% of the flies were found to be killed in each case.

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Application Example 8.

40 Each of the oil preparations obtained in Formulation Example 7 was sprayed into a glass box, (70 cm)³, containing about 50 adult oriental house flies in an amount of 0.7 ml under a pressure of 1.5 Kg/cm², and it was found that more than 80% of the flies were knocked down in 10 minutes after the treatment in each case.

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Application Example 9.

45 About 50 adult mosquitoes (*Culex pipens*) per group were released in a glass box, (70 cm)³, and sprayed with each of the oil preparations obtained in Formulation Example 6 in an amount of 0.7 ml under a pressure of 1.5 Kg/cm². It was found that more than 80% of the flies were knocked down in 10 minutes after the treatment in each case.

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Application Example 10.

50 A nylon net of about 15 mesh was sprayed on the lower part of a glass cylinder having a diameter of 20 cm and a height of 20 cm and butter was applied on the upper part of the glass cylinder to a width of about 3 cm. Then 20 adult German cockroaches were released therein. The glass cylinder containing the cockroaches was placed on another glass cylinder of the same size, and a further glass cylinder having a diameter of 20 cm and a height of 40 cm was placed thereon. 0.5 ml of each of the oil preparations obtained in Formulation Example 7 was sprayed from the upper cylinder using a glass atomizer under a pressure of 0.75 Kg/cm² and then sealed and allowed to stand. It was found that more than 90% of the cockroaches were knocked down in 30 minutes after the treatment and that more than 90% of the cockroaches were killed 3 days after the treatment.

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Application Example 11.

Insecticidal activity of each of the aerosols obtained in Formulation Example 10 on oriental house flies was tested by an aerosol test method using a Peet grady chamber [a method reported in Soap and Chemical Specialities Bluebook (1965)]. The test results revealed that knock-down of more than 80% of the flies was observed in 15 minutes after the treatment and more than 70% of the flies were killed one day after the treatment in each case.

Application Example 12.

About 50 adult mosquitoes (*Culex pipiens*) were released in a glass box, (70 cm)³, and a mosquito coil, both ends of which had been ignited, was placed in the centre of the box bottom. After 20 minutes more than 80% of the flies were found to have been knocked down.

Application Example 13.

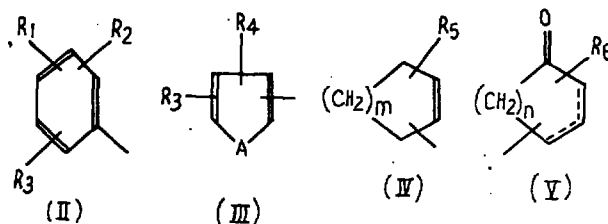
About 50 adult mosquitos (*Culex pipiens*) were released in a glass box, (70 cm)³, and a heating mat as obtained in Formulation Example 11 and fixed to an electrothermic plate was placed in the glass box followed by heating to cause the mat to smoke. Within 20 minutes, more than 90% of the mosquitoes were found to have been knocked down.

WHAT WE CLAIM IS:—

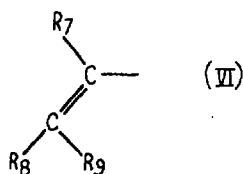
1. A substituted acetate of the following general formula (I):



wherein Y represents a group having one of the following general formulae (II) to (V):



in which R_1 and R_2 are each independently hydrogen, halogen, cyano, nitro, lower alkyl, lower alkenyl, lower alkynyl, lower alkoxy, lower alkoxyalkyl, halogen-substituted lower alkyl, halogen-substituted lower alkenyl, halogen-substituted lower alkynyl, lower alkylthio, lower alkylsulfoxyl, acyl, acyloxy, lower alkoxy carbonyl, lower alkenyloxycarbonyl, lower alkynyloxycarbonyl, or R_1 and R_2 together are methylenedioxy, tetramethylene or trimethylene; R_3 and R_4 are each independently hydrogen, halogen, cyano, nitro, lower alkyl, lower alkenyl, lower alkynyl, lower alkoxy, lower alkoxyalkyl, halogen-substituted lower alkyl, halogen-substituted lower alkenyl, halogen-substituted lower alkynyl, lower alkylthio, lower alkylsulfoxyl, acyl, acyloxy, lower alkoxy carbonyl, lower alkenyloxycarbonyl or lower alkynyloxycarbonyl; A is oxygen or sulfur; R_5 is hydrogen, halogen, cyano, nitro or lower alkyl; m is 1, 2 or 3; R_6 is hydrogen, halogen, cyano, nitro or lower alkyl; n is 1, 2 or 3; and the dotted line in the formula (V) represents a double bond present at a position conjugated or unconjugated with the ketonic group; or Y represents a substituted ethylene group of the following general formula (VI):





Application Example 11.

Insecticidal activity of each of the aerosols obtained in Formulation Example 10 on oriental house flies was tested by an aerosol test method using a Peet grady chamber [a method reported in Soap and Chemical Specialities Bluebook (1965)]. The test results revealed that knock-down of more than 80% of the flies was observed in 15 minutes after the treatment and more than 70% of the flies were killed one day after the treatment in each case.

Application Example 12.

About 50 adult mosquitoes (*Culex pipiens*) were released in a glass box, (70 cm)³, and a mosquito coil, both ends of which had been ignited, was placed in the centre of the box bottom. After 20 minutes more than 80% of the flies were found to have been knocked down.

Application Example 13.

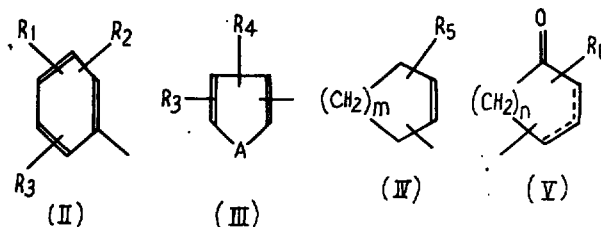
About 50 adult mosquitos (*Culex pipiens*) were released in a glass box, (70 cm)³, and a heating mat as obtained in Formulation Example 11 and fixed to an electrothermic plate was placed in the glass box followed by heating to cause the mat to smoke. Within 20 minutes, more than 90% of the mosquitoes were found to have been knocked down.

WHAT WE CLAIM IS:—

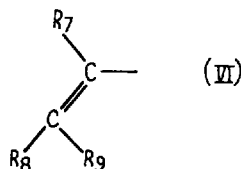
1. A substituted acetate of the following general formula (I):



wherein Y represents a group having one of the following general formulae (II) to (V):



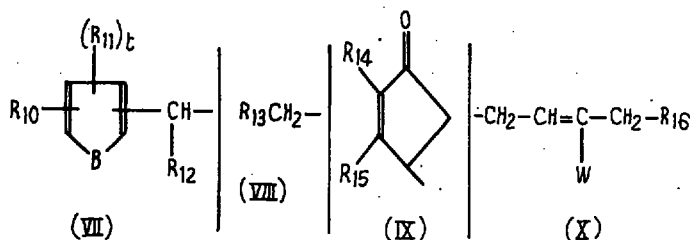
in which R_1 and R_2 are each independently hydrogen, halogen, cyano, nitro, lower alkyl, lower alkenyl, lower alkynyl, lower alkoxy, lower alkoxyalkyl, halogen-substituted lower alkyl, halogen-substituted lower alkenyl, halogen-substituted lower alkynyl, lower alkylthio, lower alkylsulfoxyl, acyl, acyloxy, lower alkoxy carbonyl, lower alkenyloxycarbonyl, lower alkynyloxycarbonyl, or R_1 and R_2 together are methylenedioxy, tetramethylene or trimethylene; R_3 and R_4 are each independently hydrogen, halogen, cyano, nitro, lower alkyl, lower alkenyl, lower alkynyl, lower alkoxy, lower alkoxyalkyl, halogen-substituted lower alkyl, halogen-substituted lower alkenyl, halogen-substituted lower alkynyl, lower alkylthio, lower alkylsulfoxyl, acyl, acyloxy, lower alkoxy carbonyl, lower alkenyloxycarbonyl or lower alkynyloxycarbonyl; A is oxygen or sulfur; R_5 is hydrogen, halogen, cyano, nitro or lower alkyl; m is 1, 2 or 3; R_6 is hydrogen, halogen, cyano, nitro or lower alkyl; n is 1, 2 or 3; and the dotted line in the formula (V) represents a double bond present at a position conjugated or unconjugated with the ketonic group; or Y represents a substituted ethylene group of the following general formula (VI):





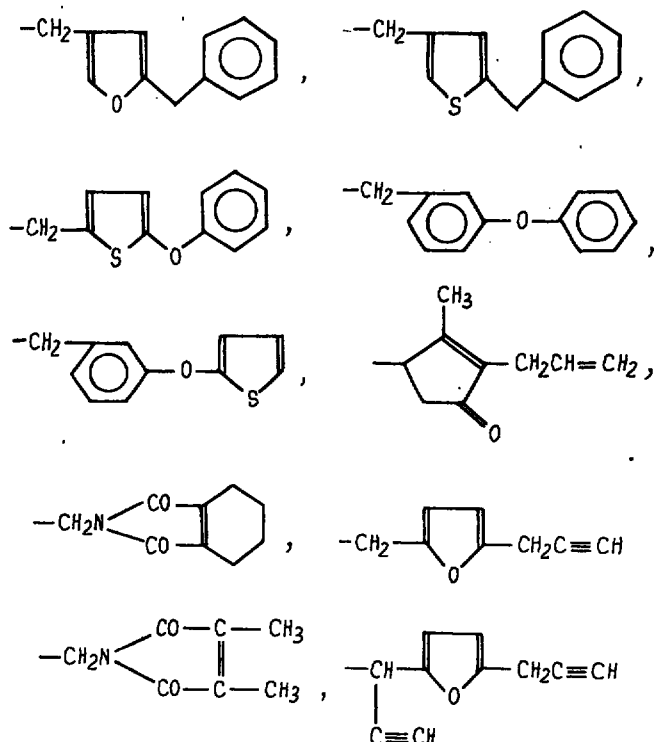
* C L M S *

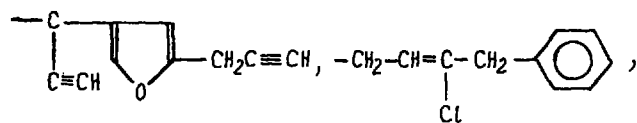
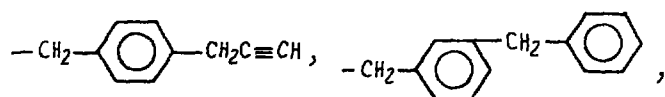
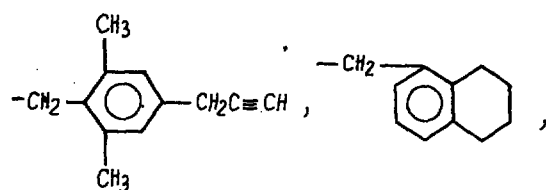
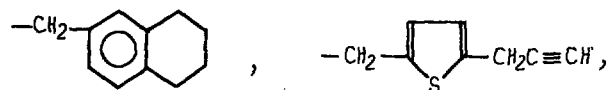
in which R_7 , R_8 and R_9 lie in a plane together with the double bond at the β,γ position of the ester group, and are each independently hydrogen, lower alkyl, lower alkenyl, lower alkynyl, halogen, acyl or acyloxy; Z is straight or branched chain lower alkyl, lower alkenyl, lower alkynyl, lower alkoxy, cyano, halogen-substituted lower alkyl, halogen-substituted lower alkenyl or C_3-C_7 alicyclic; and X represents a group having one of the following general formulae (VII) to (X):



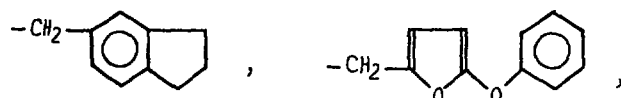
in which R_{10} is allyl, propargyl, benzyl, thenyl, furylmethyl, phenoxy or phenylthio; R_{11} is hydrogen, methyl, trifluoromethyl or halogen; or R_{10} and R_{11} may, when their terminal carbon atoms are bonded to each other, represent trimethylene or tetramethylene; R_{12} is hydrogen, ethynyl or cyano; t is 1 or 2; B is an oxygen or sulfur atom or $-CH=CH-$; R_{13} is phthalimide, thiophthalimide, di- or tetrahydrophthalimide or dialkylmaleimide; R_{14} is allyl, propargyl, benzyl or alkadienyl; R_{15} is hydrogen or methyl; R_{16} is phenyl, thienyl or furyl; and W is methyl or halogen.

2. An acetate as claimed in Claim 1, in which Y has the general formula (II), wherein R_1 is hydrogen, methoxy, ethoxy, acetoxy, methylsulfinyl, C_1-C_4 alkyl, trifluoromethyl, allyl, acetyl, ethoxycarbonyl, methylenedioxy, methylthio, trimethylene, tetramethylene, chlorine, fluorine, iodine, isopropenyl, propargyl, methoxymethyl, ethoxymethyl, chloroethylene, chloroallyl, butyryl, butylthio, allyloxycarbonyl, nitro or methoxycarbonyl; R_2 is hydrogen, methyl, methoxy, chlorine or bromine; R_3 is hydrogen or methyl; Z is C_1-C_4 alkyl, ethoxy, allyl, bromoethyl, cyclohexyl, cyclopropylmethyl, isopropenyl, propargyl, trifluoromethyl or cyano; and X is a group having one of the following formulae:

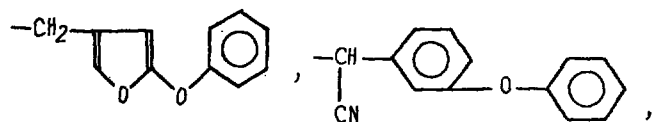
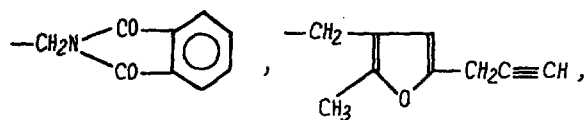
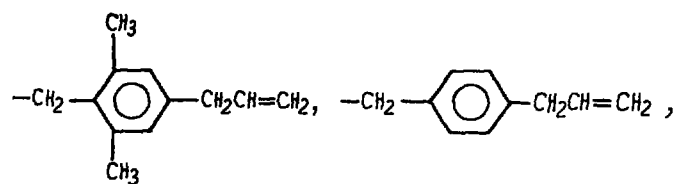
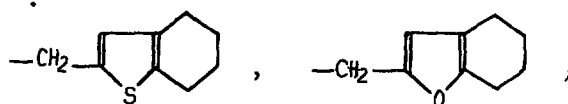




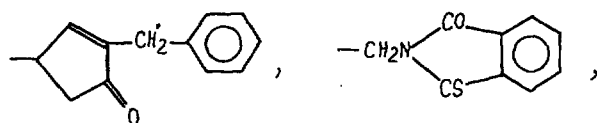
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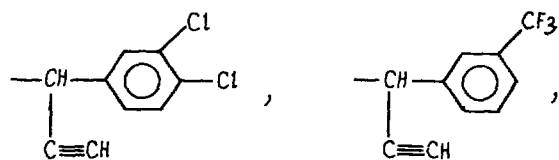
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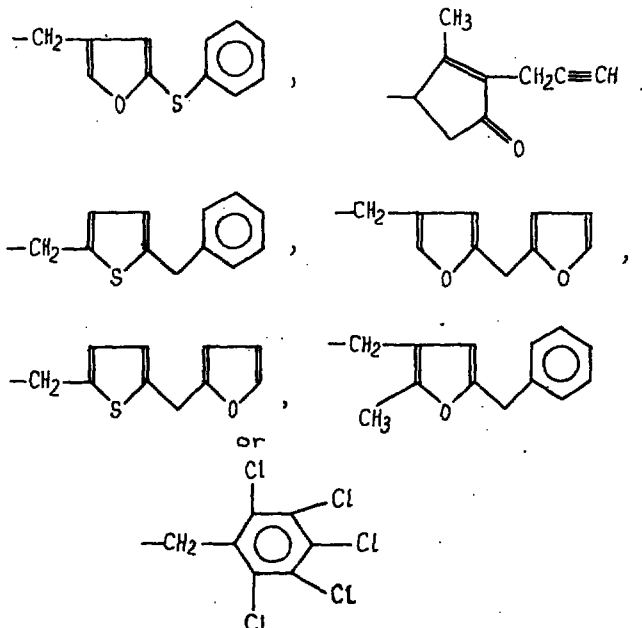


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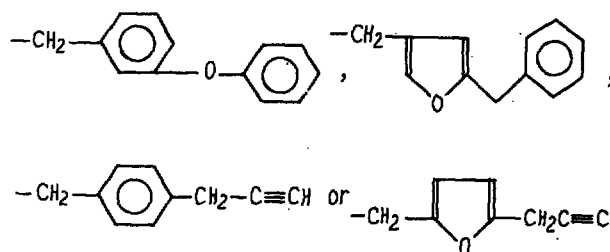




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3. An acetate as claimed in Claim 1, in which Y has the general formula (III), wherein A is sulfur and R_3 is hydrogen, methyl, allyl, methoxycarbonyl or acetyl; R_4 is hydrogen; Z is ethyl, propyl or allyl; and X is a group having one of the following formulae:

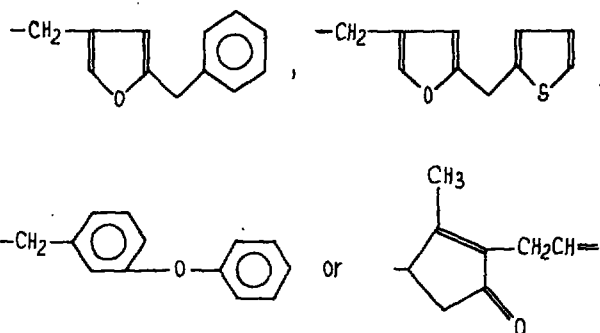
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4. An acetate as claimed in Claim 1, in which Y has the general formula (III), wherein A is oxygen and R_3 is hydrogen, methyl, allyl, methoxycarbonyl or butanoyl; R_4 is hydrogen; Z is ethyl or propyl; and X is a group having one of the following formulae:

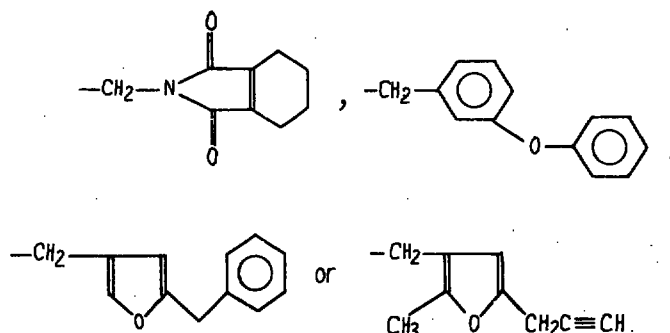
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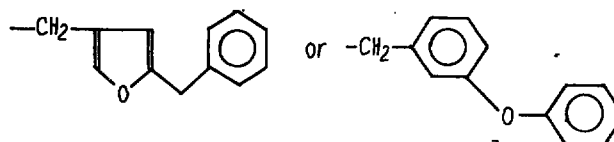
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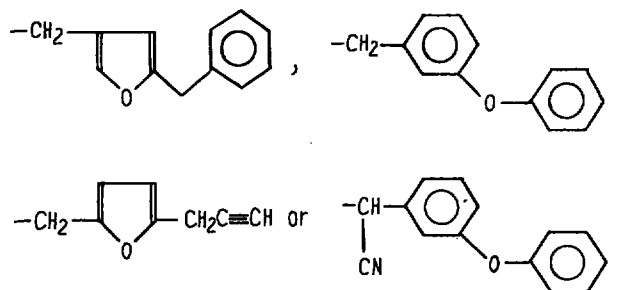
5. An acetate as claimed in Claim 1, in which Y has the general formula (IV), wherein R_5 is hydrogen or methyl; m is 1 or 2; Z is methyl, propyl, allyl or propargyl; and X is a group having one of the following formulae:



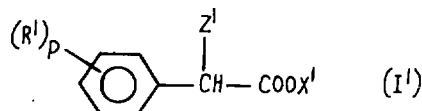
6. An acetate as claimed in Claim 1, in which Y has the general formula (V) wherein R_6 is methyl, n is 1; Z is ethyl or propyl; and X has one of the following formulae:



7. An acetate as claimed in Claim 1, in which Y has the general formula (VI), wherein R_7 is hydrogen, methyl or ethyl; R_8 is hydrogen or methyl; R_9 is methyl; Z is C_1-C_3 alkyl; and X is a group having one of the following formulae:

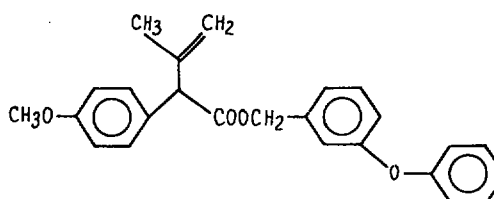


8. A compound as claimed in Claim 2 and having the following general formula (I')



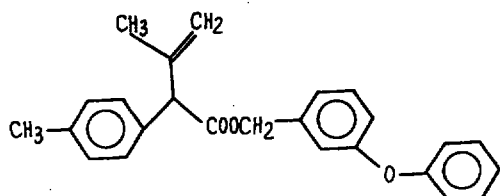
wherein R_1' is C_1-C_3 straight or branched chain alkyl, straight or branched chain C_1-C_3 alkoxy; halogen or thiomethyl or two of R_1' may together be trimethylene, tetramethylene or methylenedioxy; p is an integer of from 1 to 4; and Z' is C_3-C_3 straight or branched chain alkyl, allyl, propargyl or isopropenyl and X' is a pyrethroid alcohol residue.

9. An acetate as claimed in Claim 2 and having the formula

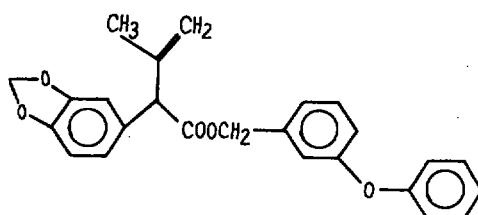




10. An acetate as claimed in Claim 2 and having the formula



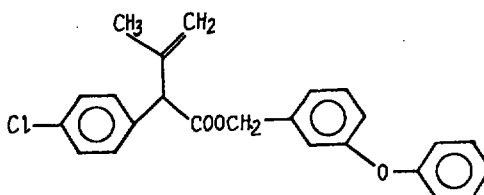
11. An acetate as claimed in Claim 2 and having the formula



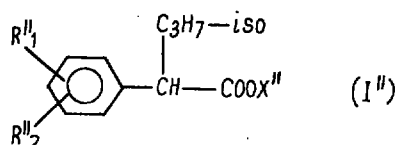
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12. An acetate as claimed in Claim 2 and having the formula

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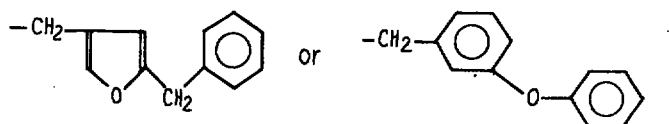
13. An acetate as claimed in Claim 2 and having the following general formula (I''):



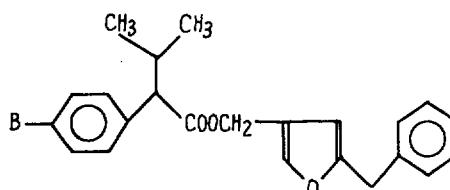
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wherein R''_1 is straight or branched chain C_1-C_4 alkyl, halogen or C_1-C_4 alkoxy; R''_2 is hydrogen or, together with R''_1 , methylenedioxy, and X'' is a group of one of the following formulae:

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14. An acetate as claimed in Claim 13 and having the general formula:



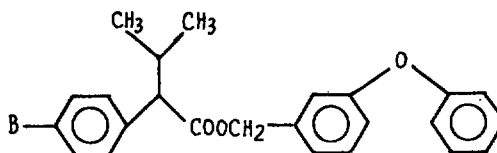
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wherein B is halogen, lower alkyl or methoxy.

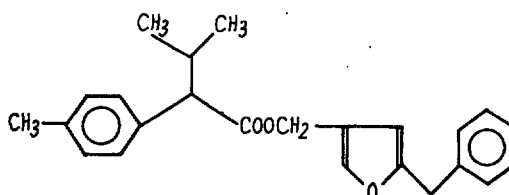


15. An acetate as claimed in Claim 13 and having the following general formula:

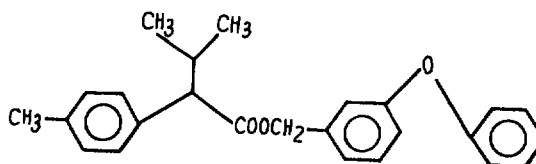


wherein B is halogen, lower alkyl or methoxy.

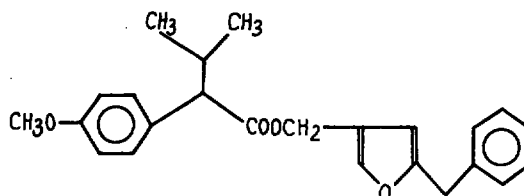
16. An acetate as claimed in Claim 13 and having the formula



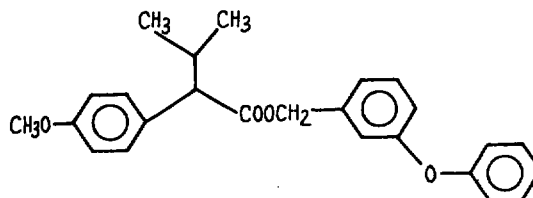
17. An acetate as claimed in Claim 13 and having the formula



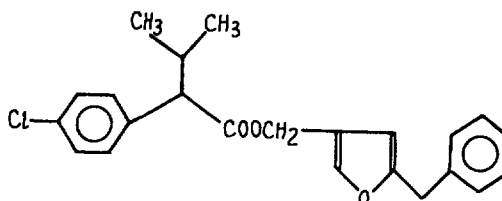
18. An acetate as claimed in Claim 13 and having the formula



19. An acetate as claimed in Claim 13 and having the formula

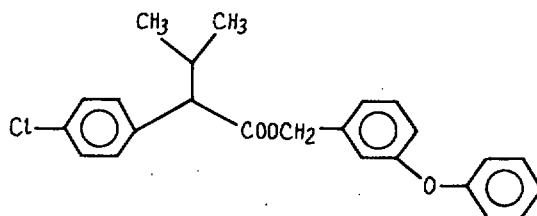


20. An acetate as claimed in Claim 13 and having the formula

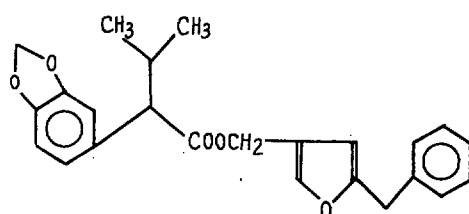




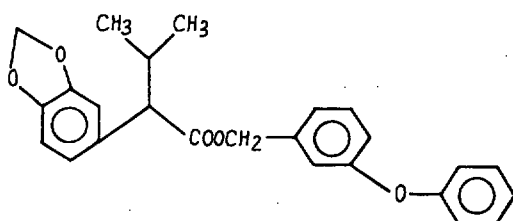
21. An acetate as claimed in Claim 13 and having the formula



22. An acetate as claimed in Claim 13 and having the formula



23. An acetate as claimed in Claim 13 and having the formula



24. An acetate being any one of the compounds identified as Compounds Nos. 1 to 300 herein excluding those compounds specifically claimed in Claims 9 to 12 and 16 to 23.

25. A process for preparing the substituted acetate of the general formula (I) as defined in Claim 1 which comprises reacting an acid represented by the following general formula (XI):



wherein Y and Z are as defined in Claim 1, or a reactive derivative thereof (as herein defined) with an alcohol represented by the following general formula (XII):



wherein X is as defined in Claim 1, or a halide or a sulphonylate thereof.

26. A process as claimed in Claim 25, wherein said reactive derivative is an acid halide, an acid anhydride, an ester with an alcohol having a low boiling point, an alkali metal salt, a silver salt or an organic tertiary base salt of an acid of the formula (XI).

27. A process as claimed in Claim 26, wherein the reaction is conducted using an acid halide of said acid in the presence of a hydrogen halide acceptor at room temperature.

28. A process as claimed in Claim 26, wherein the reaction is conducted using an ester of said acid with an alcohol having a low boiling point in the presence of an appropriate organic base catalyst.

29. A process as claimed in Claim 25 and substantially as herein described with reference to any one of esterification methods "a" to "e" herein.



30. A process as claimed in any one of Claims 25 to 29, wherein the said acid has been prepared by any one of procedures (A), (B) and (C) as herein described.

31. A process for preparing a substituted acetate of the general formula (I) as defined in Claim 1 and substantially as herein described with reference to any one of Preparations Nos. 1 to 229.

32. A substituted acetate when prepared by a process as claimed in any one of Claims 25 to 31.

33. A pesticidal composition comprising at least one substituted acetate as claimed in any one of Claims 1 to 24 and 32 and an inert carrier.

34. A pesticidal composition containing at least one substituted acetate as claimed in any one of Claims 1 to 24 and 32 and being in the form of an emulsifiable concentrate, a wettable powder, a dust, a powder, grains, granules, a coating liquid, an oil preparation, an aerosol, a mosquito coil, a smoking preparation or a fumigating preparation.

35. A pesticidal composition comprising at least one substituted acetate as claimed in any one of Claims 1 to 24 and 32 and at least one of a solvent, filler, diluent, dispersion agent, surface active agent, spreader, emulsifying agent, pressure-imparting agent, attractant, insecticide, herbicide, repellent, fertilizer, miticide, microbicide and fungicide.

36. A pesticidal composition as claimed in Claim 33 and substantially as herein described with reference to any one of Formulation Examples 1 to 12.

37. A method of treating growing crops to control insects of the Orders *Coreoptera*, *Lepidoptera*, *Diptera*, *Orthoptera*, *Hemiptera*, *Homoptera* and *Acarus* comprising applying thereto a composition as claimed in any one of Claims 33 to 36.

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