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3,829,442

INSECTICIDAL 1,3-BENZODIOXOL DERIVATIVES
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No Drawing. Filed Dec. 13, 1971, Ser. No. 207,633
Claims priority, application Switzerland, Dec. 14, 1970,
18,472/70; Sept. 17, 1971, 13,599/71; Oct. 6, 1971,
14,521/71; Nov. 11, 1971, 16,357/71

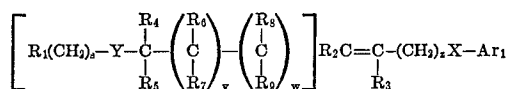
Int. Cl. C07d 13/10

U.S. Cl. 260—340.5

24 Claims

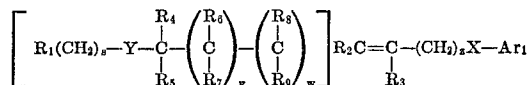
ABSTRACT OF THE DISCLOSURE

The present invention concerns novel compounds of the formula:

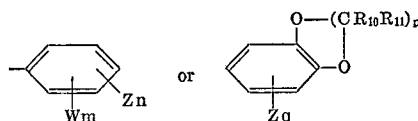


wherein R_1 to R_{11} have various significances including e.g. alkyl, X and Y include O and S and s , v and w are whole numbers and Ar_1 is phenyl or substituted phenyl. The compounds possess insecticidal properties.

The present invention relates to ethers and thioethers and more specifically to aromatic ethers and thioethers. The present invention provides compounds of formula I,



wherein Ar_1 is



wherein

W is alkyl of 1 to 5 carbon atoms, fluorine, chlorine or bromine,

Z is alkyl of 1 to 5 carbon atoms, alkenyl of 2 to 12 carbon atoms, alkoxy of 1 to 5 carbon atoms, alkenyloxy of 2 to 12 carbon atoms, formyl, alkyl carbonyl of 2 to 6 carbon atoms, alkoxy carbonyl of 2 to 6 carbon atoms, mono- or di-alkyl substituted carbamoyl each alkyl substituent being of 1 to 5 carbon atoms, alkoxy methylene of 2 to 6 carbon atoms, alkylthio of 1 to 5 carbon atoms, fluorine, chlorine, bromine, cyano or nitro,

R_{10} and R_{11} , which may be the same or different, are each hydrogen or alkyl of 1 to 5 carbon atoms, n and p , which may be the same or different, are each 1 or 2,

q is 0 or 1,

m is 0, 1, 2, 3 or 4,

R_1 is alkyl of 1 to 11 carbon atoms, non-cyclic hydrocarbon of up to 11 carbon atoms having one or two double bonds or one triple bond, cycloalkyl of 4 to 7 carbon atoms, alkyl substituted cycloalkyl of 4 to 7 ring carbon atoms the alkyl substituent having 1 to 5 carbon atoms, cycloalkenyl of 4 to 7 carbon atoms, alkyl substituted cycloalkenyl of 4 to 7 ring carbon atoms the alkyl substituent having 1 to 5 carbon atoms, phenyl, Ar_2 which has the same definition as Ar_1 above wherein Ar_1 and Ar_2 may be the same or different,

R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , R_8 and R_9 , which may be the same or different, are each hydrogen, alkyl of 1 to 5 carbon atoms or alkenyl of 2 to 6 carbon atoms,

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Y is oxygen or sulphur,

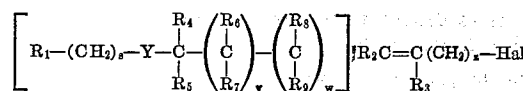
X is oxygen, sulphur, $-OCH_2-$ or $-SCH_2-$,

s , v , and w , which may be the same or different, are each 0, or 1, and

z is 1, 2 or 3.

It is to be understood that the terms alkyl, alkenyl, alkoxy and non-cyclic hydrocarbon cover both straight and branched chain configurations thereof.

The present invention also provides a process for the production of a compound of formula I, which comprises (a) Reacting a compound of formula II,

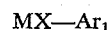


II

wherein

R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , R_8 , R_9 , Y, s , v , w and z are as defined above, and Hal is chlorine or bromine,

with a compound of formula III,



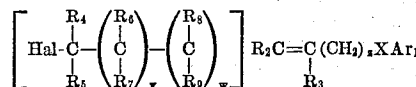
III

wherein

Ar_1 and X are as defined above, and M is hydrogen, potassium or sodium,

with the proviso that when M is hydrogen, the reaction is effected in the presence of an acid binding agent,

(b) Reacting a compound of formula IV,



IV

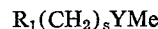
wherein

R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , R_8 , R_9 , X, Ar_1 , v and w are as defined in relation to formula I,

Hal is chlorine or bromine, and

z is 1,

with the proviso that $v+w$ is 0 or 2 or when $v+w$ is 1, R_6 and R_7 , or R_8 and R_9 are other than hydrogen, with an alcoholate or thioalcoholate of formula V,



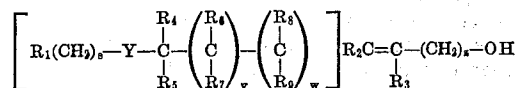
V

wherein

R_1 , Y and s are as defined in relation to formula I, and Me is sodium or potassium,

to produce a compound of formula Ia, i.e. a compound of formula I wherein z is 1, $v+w$ is 0 or 2, or when $v+w$ is 1, R_6 and R_7 , or R_8 and R_9 are other than hydrogen

(c) Condensing a compound of formula VIa,



VIa

wherein

R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , R_8 , R_9 , Y, s , v , w and z are as defined in relation to formula I,

with a compound of formula IIIa



IIIa

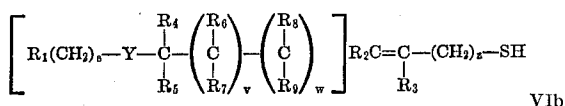
wherein

Ar_1 is as defined in relation to formula I,

in the presence of dicyclohexylcarbodiimide as condensation agent, to produce a compound of formula Ib, i.e. a compound of formula I wherein X is oxygen, or

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(d) Reacting a compound of formula VIa or Vīb,



wherein

$R_1, R_2, R_3, R_4, R_5, R_6, R_7, R_8, R_9, Y, s, v, w$ and z are as defined in relation to formula I,

or an alkali alcoholate or thioalcoholate thereof respectively with a compound of formula VII,



wherein

Ar_1 is as defined in relation to formula I, and Hal is chlorine or bromine,

with the proviso that when a compound of formula VIa or Vīb is reacted in the free alcohol or thioalcohol form thereof respectively, the reaction is effected in the presence of an acid-binding agent, to produce a compound of formula Ic i.e. a compound of formula I wherein X is $-OCH_2-$ or $-SCH_2-$.

The production of compounds of formula I in accordance with process (a) may be effected as follows viz.

A compound of formula III is conveniently reacted in a solvent, for example, a hydrocarbon such as benzene, an ether such as dioxane, 1,2-dimethoxyethane, diethyleneglycol-dimethyl ether, an alcohol such as ethanol, tert. butanol, a ketone such as acetone, a nitrile such as acetonitrile, an acid amide such as dimethylformamide, or in an appropriate solvent mixture, in the presence of an acid binding agent, for example, sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, potassium-tert.butoxide, at a temperature between preferably 0° and about 100° C. with a compound of formula II. Potassium iodide may, conveniently be added in catalytic amounts to the reaction mixture as catalyst.

When z of formula I is 2, reaction conditions which may cause a β -elimination, e.g. the use of sodium or potassium hydroxide, in e.g. dimethylformamide as solvent, are avoided.

Working up of the reaction product is effected in the usual manner.

The production of compounds of formula Ia in accordance with process (b) may be effected as follows viz.

A compound of formula IV is reacted, conveniently in an appropriate reaction medium, for example an ether such as dioxane, 1,2-dimethoxyethane, diethyleneglycol-dimethyl ether, a hydrocarbon such as benzene, or provided that Y in formula V signifies oxygen, in an alcohol of formula $R_1(CH_2)_sOH$ wherein R_1 and s correspond to those of formula V, or provided that Y in formula V signifies sulphur, in a mercaptan of formula $R_1(CH_2)_sSH$ wherein R_1 and s correspond to those of formula V, preferably at a temperature between room temperature and about 100° C., over a period, e.g. 3 to 15 hours, with a compound of formula V. Working up of the reaction product is effected in the usual manner.

The production of compounds of formula Ib in accordance with process (c) may be effected as follows viz.

A compound of formula VIa or Vīb is reacted, conveniently in an appropriate solvent, for example a hydrocarbon such as benzene, an ether such as 1,2-dimethoxyethane, an alcohol such as ethanol or tert.butanol, a ketone such as acetone, a nitrile such as acetonitrile, an acid amide such as dimethyl formamide, or in an appropriate solvent mixture, in the presence of an acid binding agent, for example sodium hydroxide and potassium hydroxide, at a temperature between 20° and 100° C. with a compound of formula VII. Working up of the reaction product is effect in conventional manner.

When the compounds of formula VIa and Vīb are reacted in the form of an alkali alcoholate or thioalcoholate, the reaction may be effected in the absence of an acid

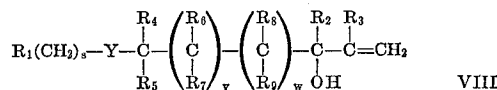
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binding agent. The reaction may be effected in an appropriate solvent, such as benzene, tert.butanol, 1,2-dimethoxyethane, dimethylformamide. Working up is effected in the usual manner.

The compounds of formula I are generally colourless oils or crystalline and may be characterized in the usual manner.

The compounds of formula II employed as starting material in the production of compounds of formula I in accordance with process (a) above, may be produced by a process as follows viz.

(a') Reacting a compound of formula VIII,

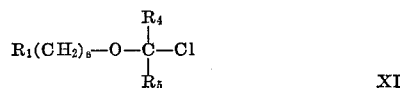


wherein

$R_1, R_2, R_3, R_4, R_5, R_6, R_7, R_8, R_9, Y, s, v$, and w are as defined in relation to formula I,

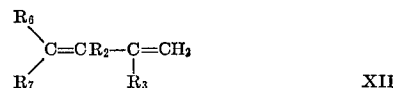
with a halide transmitter e.g. hydrobromic acid, thionyl halides or a suitable phosphorous halide in the presence of an acid binding agent to obtain a compound of formula IIa i.e. a compound of formula II, wherein z is 1.

(b') Reacting a compound of formula XII,



wherein

R_1, R_4, R_5 and s are as defined in relation to formula I, with a compound of formula XII,

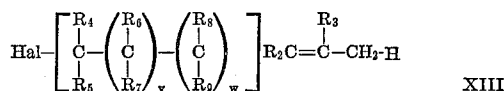


wherein

R_2, R_3, R_6 and R_7 are as defined in relation to formula I, if required, in the presence of an appropriate catalyst, such as anhydrous zinc chloride, to produce a compound of formula IIb i.e. a compound of formula II wherein Y is oxygen, Hal is chlorine, z and v are 1 and w is 0.

(c') Reacting a compound of formula VIa, wherein z is 3, with an appropriate halide transmitter e.g. hydrobromic acid, a thionylhalide or a suitable phosphorous halide in the presence of an acid binding agent, to produce a compound of formula IIc i.e. a compound of formula II, wherein z is 3.

(d') Reacting a compound of formula XIIIa,



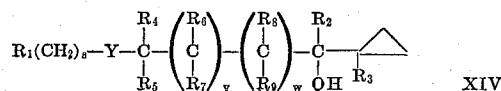
wherein

R_2, R_3 are as defined in relation to formula I, Hal is chlorine or bromine,

each of R_4, R_5, R_6, R_7, R_8 , and R_9 is hydrogen, and each of v and w is 0 or 1,

with a compound of formula V, to produce a compound of formula IId i.e. a compound of formula II, wherein R_4 and R_5 is hydrogen, and each of v and w is 0.

(e') Reacting a compound of formula XIV,



wherein

$R_1, R_2, R_3, R_4, R_5, R_6, R_7, R_8, R_9, Y, s, v$, and w are as defined in relation to formula I,

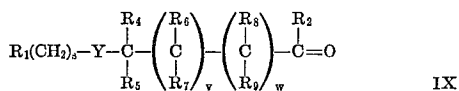
with concentrated hydrochloric or hydrobromic acid, preferably of 48% by weight concentration, to produce a compound of formula IIe i.e. a compound of formula II, wherein z is 2 and Hal is chlorine or bromine.

The production of compounds of formula IIa in accordance with process (a') may be effected as follows viz.

The reaction temperature and solvent depend on the halide transmitter employed. Thus, with 48% by weight hydrogen bromide or hydrochloric acid no solvent is required and the reaction temperature may be between -20° and 0° C. With thionylhalides, a suitable solvent is ether and a suitable reaction temperature is room temperature. With phosphorous halides, e.g. phosphorous tribromide, pyridine may be employed as solvent which also serves as acid binding agent and a suitable reaction temperature is between -20° and 0° C.

The purification of the resulting compound of formula IIa may, if desired be omitted, and the compound may be employed directly in the production of compounds of formula I in accordance with process (a) above.

The compounds of formula XIII employed as starting material in process (a') above may, for example, be produced by reacting a compound of formula IX,



wherein

$R_1, R_2, R_4, R_5, R_6, R_7, R_8, R_9, Y, s, v$, and w are as defined in relation to formula I,

with a compound of formula X,



wherein

R_3 is as defined above, and

Mt is $-MgCl$, $-MgBr$ or Li in organometallic bond,

in an appropriate solvent, such as tetrahydrofuran, and subsequent hydrolysis of the resulting magnesium or lithium compound in the usual manner.

The compounds of formulae IX and X employed in the production of compounds of formula VIII above are known or may be produced in accordance with known methods.

The production of compounds of formula IIb in accordance with process (b') may be effected as follows viz.

The reaction may be effected with or without a solvent. An example of a suitable solvent is ether. The reaction temperature may vary between 0° and 30° C.

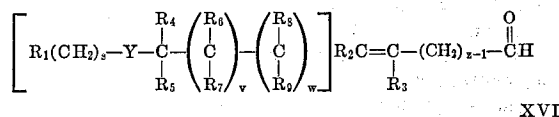
The starting compounds of formulas XI and XII employed in process (b') above are either known or may be produced in accordance with known methods.

The production of compounds of formula IIc in accordance with process (c') above may be effected as follows viz.

The reaction conditions will vary with the actual halide transmitter employed. Thus, with 48% by weight hydrogen bromide no solvent is required and a suitable reaction temperature is between -20° and 0° C. With thionylhalides a suitable solvent is ether or benzene and a suitable reaction temperature is between -10° and 25° C. With phosphorous halides e.g. phosphorous tribromide, a suitable solvent and acid binding agent is pyridine the reaction temperature varying between -20° C. and room temperature.

The starting compounds of formula VIa, wherein z is 3 employed in process (c') and also in process (c) above

for the production of some of the compound of formula Ib and in process (d) above for the production of some of the compounds of formula Ic, may be produced by sodium bromohydrate reduction of a compound of formula XVI,



wherein

$R_1, R_2, R_3, R_4, R_5, R_6, R_7, R_8, R_9, Y, s, v$ and w are as defined in relation to formula I, and z is 3,

in manner known *per se*.

The compounds of formula XVI, may, for example, be obtained by reacting the compounds of formula VIII with alkyl vinyl ethers in the presence of mercury-II-acetate at an elevated temperature, preferably for a period of e.g. 4 days, and subsequent transposition by short heating to $160-190^\circ$ C., preferably over 1 to 2 hours.

The production of compounds of formula IIId in accordance with process (d') may be effected as follows viz. The compounds of formulae V and XIIIa are dissolved in a suitable solvent e.g. an alcohol of formula $R_1(CH_2)_sOH$ or thioalcohol of formula $R_1(CH_2)_sSH$ wherein R_1 and s correspond to those of formula V, and acid amide e.g. dimethyl formamide, or a sulphoxide e.g. dimethyl sulphoxide and the reaction is effected at a temperature of between 0° and 100° C. preferably between 20° and 30° C.

The starting compounds of formula XIIIa employed in process (d') above are either known or may be produced in accordance with known methods.

The production of compounds of formula IIe in accordance with process (e') may be effected as follows:

The compound of formula XIV and either 48% by weight hydrogen bromide or concentrated hydrochloric acid are reacted at a temperature of about 0° C. A solvent is not required.

The compounds of formula XIV employed as starting material in process (e') above may be produced by reacting a compound of formula IX with a Grignard compound of formula XV,



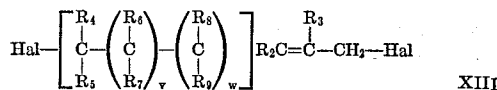
wherein

R_3 is as defined in relation to formula I,

and subsequent hydrolysis of the magnesium compound.

The compounds of formula III employed as a starting material in process (a) above for the production of compounds of formula I, are known.

The compounds of formula IV, employed as a starting material in process (b) above for the production of compounds of formula Ia may be produced by reacting a compound of formula XIII,



wherein

$R_2, R_3, R_4, R_5, R_6, R_7, R_8, R_9, v$ and w are as defined in relation to formula I, and

Hal is chlorine or bromine, with a compound of formula III, with the proviso that when M of formula III is hydrogen, the reaction is effected in the presence of an acid binding agent.

The compounds of formula V employed as a starting material in process (b) above for the production of compounds of formula Ia are known or may be produced in accordance with known methods.

The compounds of formula VIa employed as a starting material in processes (b) and (d) above for the production of compounds Ib and Ic respectively, when z is 3 has already been described. The production of compounds of formula VIa when z is 1 or 3 may be effected by reacting a compound of formula II, wherein z is 1 or 3, with aqueous alkali e.g. potassium hydroxide in manner known *per se*.

The compounds of formula VIa when z is 2 may be effected by reacting a compound of formula II wherein z is 2 with potassium acetate, preferably in glacial acetic acid under reflux and hydrolysing the resulting acetate with methanolic potassium hydroxide.

The compound of formula VIb employed as a starting material in process (d) above for the production of some of the compounds of formula Ic, wherein z is 1 or 3 may be produced as follows viz.

Reacting a compound of formula II, wherein z is 1 or 3 with thiourea or ammonium dithiocarbamate in water at about 100° C. and subsequent alkaline hydrolysis of the resulting compound with e.g. 5N potassium hydroxide.

The compounds of formula VIb, wherein z is 2 may, for example, be produced by reacting a compound of formula II, wherein z is 2 with an alkali thioacetate e.g. potassium thioacetate, in e.g. dimethyl sulphoxide or acetonitrile, as solvent followed by alkaline hydrolysis e.g. with methanolic potassium hydroxide.

The compounds of formula I are useful because they exhibit an inhibiting effect on the development of the insects.

Dysdercus fasciatus (Egyptian cotton worm)

Prodenia littura (cotton stainer)

Tenebrio molitor (flour beetle) and

Tetranychus urticae (red spider)

from one development stage thereof to the next, to result either in death or reduced oviposition or inhibition of copulation as indicated by the following tests viz.

TEST 1

Insecticidal effect on *Dysdercus fasciatus* larvae (Egyptian cotton worm)

Filter paper is impregnated with a solution of a compound of formula I. A box made from polystyrene (200 x 10 x 85 mm.) is coated with the filter paper treated in this way. A folded filter paper which is also impregnated and covered with about 30 *Dysdercus* larvae of the 4th larval stage is placed into this box. Pounded cotton seeds as food and a drinking-vessel are placed into it. The number of adults which have developed normally after 14 to 15 days is determined.

TEST 2

Effect on the development of *Prodenia littura* larvae (cotton stainer) into adults

Filter paper is impregnated with a solution of a compound of formula I. Partitions, having a size of 3.5 x 5.5 cm., of a plastic box are coated with the filter paper treated in this way. One *Prodenia* caterpillar in the third to fourth larval stage is placed into each partition and a piece of artificial medium is given as food. The insects are kept at 25°. The number of the adults which have developed normally after 21 days is determined.

TEST 3

Effect on the development of *Tenebrio molitor* chrysales (flour beetle) into adults

A compound of formula I is used at a concentration of 1% by weight in acetic solution. 2 μ l. of the resulting solution, corresponding to 20 micrograms of compound, are applied on the abdominal side of the last three segments of young chrysales (not older than 18 hours) by means of a 1-microlitre bulb pipette. 10 chrysales are used for each test. The treated chrysales are kept at 28°

in plastic cups. The adults which have developed normally are counted after 10 to 12 days.

TEST 4

Contact effect in *Tetranychus urticae* (red spider)

One day before treatment 10 adult females of *Tetranychus urticae* are placed by means of a pencil between two rings (diameter: 3 cm.) of caterpillar lime which are applied to a leaf of a cotton plant. The cotton leaves are sprayed to run off by means of a sprayer with a liquor containing 0.1% by weight of a compound of formula I. After drying, the plants are kept at room temperature and in light. The dead and live insects are counted 6 days after the treatment. The relation between the treated and one untreated population shows the effect.

From LD₅₀ oral or dermal determinations on the male rat, a low toxicity of the compounds of formula I towards warm blooded animals is indicated.

For the above-mentioned use, the amount applied to a locus to be treated e.g. a plant culture, will of course vary depending on the compound employed, the mode of application, ambient conditions, and the insects to be combated. However, in general satisfactory results are obtained when a compound of formula I is applied to the locus in an amount between 1 and 10 kg./hectare, the application being repeated as required.

The compounds may be applied to the locus with conventional applicator equipment and by conventional methods e.g. strewing, spraying and dusting.

Compositions may be produced in conventional manner and may comprise a compound of formula I in admixture with insecticidal carriers e.g. talc, diatomaceous earth, bentonite and pumice, insecticidal diluents e.g. water or appropriate organic solvents such as alcohols, petroleum and tar distillates and/or insecticidal adjuvants e.g. emulsifying agents, solvent aids such as mineral oils and wetting and adhesive agents such as cellulose derivatives.

Concentrate forms of the compositions may generally contain between 2 and 90%, preferably between 5 and 50% by weight, of a compound of formula I.

Application forms of the composition may generally contain between 0.01 and 0.1%, by weight of a compound of formula I.

Preferred compounds of formula I are as follows:

- 5-(5-tert.butoxy-3-methyl-2-pentenyl)-1,3-benzodioxol,
- 5-(5-isopropylthio-3-methyl-2-pentenyl)-1,3-benzodioxol,
- 4-(3-ethyl-5-sec.butoxy-2-pentenyl)-benzoic methyl ester,
- 4'-(3-ethyl-5-sec.butoxy-2-pentenyl)-acetophenone,
- 5-(5-cyclopentyl-3-methyl-2-pentenyl)-1,3-benzodioxol,
- 5-[3-methyl-5-(2-pentenyl)-2-pentenyl]-1,3-benzodioxol,
- 5-[(5-isopropoxy-3-methyl-2-pentenyl)-methyl]-1,3-benzodioxol,
- 5-(5-isopropoxy-3-methyl-2-pentenyl)-1,3-benzodioxol,
- 4-(5-isopropoxy-3-methyl-2-pentenylthio)-chlorobenzene,
- 4-(5-isopropoxy-3-methyl-2-pentenyl)-thioanisole,
- 4-(5-isopropoxy-3-methyl-2-pentenyl)-ethylbenzene,
- 5-(5-ethoxy-3-methyl-2-pentenyl)-1,3-benzodioxol,
- 4-(6-ethoxy-3-methyl-2-hexenyl)-benzoic acid methyl ester,
- 4'-(6-ethoxy-3-methyl-2-hexenyl)-acetophenone,
- 5-(4-isobutoxy-2-methyl-2-butenyl)-1,3-benzodioxol,
- 5-(6-isopropoxy-4-methyl-3-hexenyl)-1,3-benzodioxol.

The following Examples illustrate the production of the compounds of formula I, but in no way limit the invention. The temperatures are indicated in degrees Centigrade. Where concentration is indicated as a percent, this is percent by weight.

EXAMPLE 1

2-(3-Ethyl-5-sec.butoxy-2-pentenyl-oxo)-benzaldehyde
(according to process (a))

9.3 g. (0.05 mol) of 3-ethyl-5-sec.butoxy-1-penten-3-ol are added dropwise at 5° in the course of 15 minutes and while stirring to 20 cc. of 48% hydrobromic acid. After stirring the mixture vigorously at 5 to 10° for half an hour it is extracted with ether, the ether extract is extracted with 10% soda solution and subsequently with saturated solution of sodium chloride, is dried with potassium carbonate and concentrated by evaporation. The resulting

1-bromo-3-ethyl-5-sec.butoxy-2-pentene is added without purification to 6.1 g. (0.05 mol) of salicylic aldehyde and 2.8 g. (0.05 mol) of potassium hydroxide in 80 cc. of 1,2-dimethoxy ethane. The mixture is stirred at 20-25° for 24 hours, is subsequently filtered and concentrated by evaporation at reduced pressure. The residue is taken up in ether, extracted with icy cold 10% sodium hydroxide solution and subsequently with saturated salt solution, is dried with sodium sulphate and evaporated.

The obtained 2-(3-ethyl-5-sec.butoxy-2-pentenyl-oxo)-benzaldehyde may be purified by chromatography on silica gel with hexane/ethyl acetate 1:1 as elant. n_D^{20} : 1.5090.

Analysis: $C_{18}H_{26}O_3$ (molecular weight: 290.4). Calc.: C, 74.4%; H, 9.0%. Found: C, 74.1%; H, 9.2%.

In analogous manner as described in Example 1 but using the starting compound of formula VIII, indicated in the following Table, the following compounds of general formula I are obtained.

Example		Empirical formula	Molecular weight	n_D^{20}	Analysis percent, calc./found			Starting compound of formula III produced in example No.
					C	H	S	
2.....	2-(3-ethyl-5-isopropoxy-2-pentenyl)oxy)benzaldehyde.....	$C_{17}H_{24}O_3$	276.4	1.5194	73.9 73.5	8.8 9.1	64	
3.....	4-(3-ethyl-5-isopropoxy-2-pentenyl)oxy)benzaldehyde.....	$C_{17}H_{24}O_3$	276.4	1.5290	73.9 74.3	8.8 8.8	64	
4.....	5-(3-ethyl-5-sec.butoxy-2-pentenyl)oxy)-1,3-benzodioxol.....	$C_{18}H_{24}O_4$	306.4	1.5104	70.6 70.1	8.6 8.1	66	
5.....	5-(3-ethyl-5-isopropoxy-2-pentenyl)oxy)-1,3-benzodioxol.....	$C_{17}H_{24}O_4$	292.4	1.5128	69.8 69.0	8.3 8.7	64	
6.....	5-(5-tert.butoxy-3-methyl-2-pentenyl)oxy)-1,3-benzodioxol.....	$C_{17}H_{24}O_4$	292.4	1.5124	69.8 69.3	8.3 8.0	67	
7.....	5-(5-isopropylthio-3-methyl-2-pentenyl)oxy)-1,3-benzodioxol....	$C_{18}H_{22}O_3S$	294.4	1.5481	65.4 65.8	7.5 7.8	10.9 11.0	68
8.....	5-(5-cyclohexyloxy-3-methyl-2-pentenyl)oxy)-1,3-benzodioxol....	$C_{19}H_{26}O_4$	318.4	1.5310	71.7 71.9	8.2 8.4	70	
9.....	4-(3-ethyl-5-sec.butoxy-2-pentenyl)oxy)benzoic methyl ester....	$C_{18}H_{20}O_4$	320.4	1.5114	71.2 71.5	8.8 8.9	66	
10.....	4-(3-ethyl-5-isopropoxy-2-pentenyl)oxy)benzoic methyl ester....	$C_{18}H_{24}O_4$	306.4	1.5153	70.6 70.7	8.6 8.9	64	
11.....	4-(5-tert.butoxy-3-methyl-2-pentenyl)oxy)benzoic methyl ester..	$C_{18}H_{24}O_4$	306.4	1.5143	70.6 70.9	8.6 8.9	67	
12.....	4-(5-isopropylthio-3-methyl-2-pentenyl)oxy)benzoic methyl ester.	$C_{17}H_{24}O_3S$	308.4	1.5461	66.2 66.1	7.8 8.1	10.4 10.5	68
13.....	4'-(3-ethyl-5-sec.butoxy-2-pentenyl)oxy)acetophenone.....	$C_{18}H_{20}O_3$	304.4	1.5214	75.0 75.0	9.3 9.4	66	
14.....	4-(5-cyclohexyloxy-3-methyl-2-pentenyl)oxy)-benzoic acid-methylester.	$C_{20}H_{26}O_4$	332.4	1.5299	72.3 72.7	8.5 8.8	70	
15.....	4'-(3-ethyl-5-sec.butoxy-2-pentenyl)oxy)-butyrophenone.....	$C_{21}H_{22}O_3$	332.5	1.5154	75.9 76.4	9.7 9.8	66	
16.....	4-(3-ethyl-5-sec.butoxy-2-pentenyl)oxy)-benzoic acid-isopropyl-ester.	$C_{21}H_{22}O_4$	348.5	1.5037	72.4 72.6	9.3 9.5	66	
17.....	5-(5-cyclopentyloxy-3-methyl-2-pentenyl)oxy)-1,3-benzodioxol....	$C_{18}H_{24}O_4$	304.4	1.5301	71.0 71.3	7.9 8.1	71	
18.....	5-[3-methyl-5-(3-pentyloxy)-2-pentenyl]oxy)-1,3-benzodioxol....	$C_{18}H_{24}O_4$	306.4	1.5118	70.6 70.9	8.6 8.6	73	
19.....	5-[3-methyl-5-(2-pentyloxy)-2-pentenyl]oxy)-1,3-benzodioxol....	$C_{18}H_{24}O_4$	306.4	1.5080	70.6 70.5	8.6 8.9	72	
20.....	5-(5-ethoxy-3-methyl-2-pentenyl)oxy)-1,3-benzodioxol.....	$C_{18}H_{20}O_4$	264.3	1.5240	68.2 68.3	7.6 7.5	75	
21.....	5-(5-n.butoxy-3-methyl-2-pentenyl)oxy)-1,3-benzodioxol.....	$C_{17}H_{24}O_4$	292.4	1.5142	69.8 69.1	8.3 8.3	74	
22.....	5-[3-methyl-5-(6-methyl-5-hepten-2-yloxy)-2-pentenyl]oxy)-1,3-benzodioxol.	$C_{21}H_{30}O_4$	346.5	1.5160	72.8 73.0	8.7 9.0	77	
23.....	4'-(5-ethoxy-3,5-dimethyl-2-hexenyloxy)-acetophenone.....	$C_{18}H_{26}O_3$	290.4	1.5263	74.4 74.4	9.0 8.9	76	

EXAMPLE 24

5-(5-Isopropoxy-3-methyl-2-pentenylthio)-1,3-benzodioxol (according to process (a))

1.7 g. (0.03 mol) of pulverised potassium hydroxide are added to a solution of 4.1 g. (0.03 mol) of 3,4-methylendioxy-phenol and 6.2 g. (0.035 mol) of 1-chloro-5-isopropoxy-3-methyl-2-pentene in 100 cc. of 1,2-dimethoxyethane. The mixture is stirred at 60° for a period of 18 hours, is subsequently filtered and evaporated at reduced pressure. The residue is dissolved in ether, washed with 5% solution of sodium hydroxide and subsequently with saturated salt solution, dried with sodium sulphate and evaporated.

The remaining 5-(5-isopropoxy-3-methyl-2-pentenylthio)-1,3-benzodioxol is purified by chromatography on silica gel with hexane/ethyl acetate 9:1. A chromatographically uniform and colourless oil is obtained which according to gas-chromatogramme and NMR-spectrum consists of a mixture of 30% of the 2-cis and 70% of the 2-trans compound. $n_D^{20}=1.5167$.

Analysis: $C_{16}H_{22}O_4$ (molecular weight: 278.3). Calc.: C, 69.0%; H, 7.9%. Found: C, 68.5%; H, 7.9%.

In analogous manner as described in Example 24, but using the starting compounds of formula III indicated in the following Table, the following compounds of general formula I are obtained:

Example		Empirical formula	Molecular weight	n_D^{20}	Analysis percent, calc./found						Starting compound of formula III
					C	H	Br	Cl	N	S	
25	2-(5-isopropoxy-3-methyl-2-pentenylthio)-benzoic acid-methylester.	$C_{17}H_{24}O_3S$	308.4	1.5492	66.2 66.9	7.8 7.9	----- -----	----- -----	10.4 10.4	2-mercaptobenzoic acid-methylester.	
26	3-(5-isopropoxy-3-methyl-2-pentenylthio)-bromobenzol.	$C_{15}H_{21}BrO_2$	313.2	1.5138	57.5 58.1	6.8 7.0	25.5 25.1	----- -----	----- -----	3-bromophenol.	
27	4-(5-isopropoxy-3-methyl-2-pentenylthio)-chlorobenzol.	$C_{15}H_{21}ClOS$	284.8	1.5332	63.3 63.1	7.4 7.6	----- -----	12.4 13.0	11.3 10.6	4-chlorophenol.	
28	4-(5-isopropoxy-3-methyl-2-pentenylthio)-anisole.	$C_{16}H_{24}O_3$	264.4	1.5050	72.7 72.3	9.2 9.5	----- -----	----- -----	----- -----	4-methoxyphenol.	
29	4-(5-isopropoxy-3-methyl-2-pentenylthio)-thioanisole.	$C_{16}H_{24}O_2S$	280.4	1.5329	68.5 68.0	8.6 8.6	----- -----	----- -----	11.4 10.9	4-(methylthio)-phenol.	
30	4-(5-isopropoxy-3-methyl-2-pentenylthio)-ethylbenzol.	$C_{17}H_{26}O_2$	262.4	1.4992	77.8 77.5	10.0 10.7	----- -----	----- -----	----- -----	4-ethylphenol.	
31	4-(5-isopropoxy-3-methyl-2-pentenylthio)-nitrobenzol.	$C_{15}H_{21}NO_4$	279.3	1.5335	64.5 64.4	7.6 7.7	----- -----	----- -----	5.0 4.8	4-nitrophenol.	
32	4-(5-isopropoxy-3-methyl-2-pentenylthio)-1,3-dichlorobenzol.	$C_{15}H_{20}Cl_2O_2$	303.2	1.5244	59.4 59.4	6.6 6.6	----- -----	23.4 23.6	----- -----	2,4-dichlorophenol.	

EXAMPLE 33

5-(6-Ethoxy-3-methyl-2-hexenyloxy)-1,3-benzodioxol (according to process (a))

2.21 g. (0.01 mol) of 6-ethoxy-1-bromo-3-methyl-2-hexene are added at 5° and while stirring to 1.38 g. (0.01 mol) of 3,4-methylendioxyphenol and 0.56 g. (0.01 mol) of potassium hydroxide in 50 cc. of 1,2-dimethoxyethane. After stirring at 5° for 2 hours the mixture is stirred at 20-25° during the course of 60 hours, is subsequently filtered and the filtrate is evaporated at reduced pressure. The residue is taken up in ether, is washed with water, dried with sodium sulphate, and the ether is distilled off. After chromatography of the residue on silica gel with hexane/ethyl acetate 9:1, 5-(6-ethoxy-3-methyl-2-hexenyloxy)-1,3-benzodioxol is obtained as colourless oil. $n_D^{20}=1.5192$.

Analysis: $C_{16}H_{22}O_4$ (molecular weight: 278.3). Calc.: C, 69.0%; H, 8.0%. Found: C, 68.9%; H, 8.1%.

In analogous manner as described in Example 33, but using 4-hydroxy-benzoic acid-methyl ester in the place of 3,4-methylendioxyphenol, the following compound of general formula I is produced:

EXAMPLE 34

4-(6-Ethoxy-3-methyl-2-hexenyloxy)-benzoic methyl ester

$n_D^{20}=1.5202$.

Analysis: $C_{17}H_{24}O_4$ (molecular weight: 292.4). Calc.: C, 69.8%; H, 8.3%. Found: C, 69.5%; H, 8.2%.

In analogous manner as described in Example 33, but using p-hydroxy-acetophenone in the place of 3,4-methylendioxy-phenol, the following compound of general formula I is produced:

EXAMPLE 35

4'-(6-Ethoxy-3-methyl-2-hexenyloxy)-acetophenone

$n_D^{20}=1.5266$.

Analysis: $C_{17}H_{24}O_3$ (molecular weight: 276.4). Calc.: C, 73.9%; H, 8.8%. Found: C, 73.5%; H, 8.8%.

EXAMPLE 36

5-(4-Isobutoxy-2-methyl-2-butenyloxy)-1,3-benzodioxol (according to process (a))

2.21 g. (0.01 mol) of 1-bromo-4-isobutoxy-2-methyl-2-butene are added at 0° during the course of 5 minutes to 1.38 g. (0.01 mol) of 3,4-methylendioxy-phenol and 0.56 g. (0.01 mol) of potassium hydroxide in 40 cc. of 1,2-dimethoxyethane. After stirring the reaction mixture at room temperature for 24 hours it is filtered and the solvent is distilled off at reduced pressure. The residue is dissolved in ether, washed with saturated salt solution, dried with sodium sulphate and evaporated. The residue is purified by chromatography on silica gel with hexane/ethyl acetate 9:1. 5-(4-isopropoxy-2-methyl-2-butenyloxy)-1,3-benzodioxol is obtained as colourless oil. $n_D^{20}=1.5150$.

Analysis: $C_{16}H_{22}O_4$ (molecular weight: 278.3). Calc.: C, 69.0%; H, 8.0%. Found: C, 69.0%; H, 8.3%.

EXAMPLE 37

5-(6-Isopropoxy-4-methyl-3-hexenyloxy)-1,3-benzodioxol (according to process (a))

2.35 g. (0.017 mol) of potassium carbonate and 50 mg. of potassium iodide are added to a solution of 4.0 g. (0.017 mol) of 1-bromo-6-isopropoxy-4-methyl-3-hexene and 2.35 g. (0.017 mol) of 3,4-methylendioxy-phenol in 120 cc. of acetone. The suspension is boiled under reflux during the course of 20 hours, is then filtered and liberated from acetone in a vacuum. The residue is taken up in ether, washed with water and saturated salt solution, dried over sodium sulphate and evaporated. The residue is chromatographed on silica gel with hexane/ethyl acetate 9:1. Thus the cis/trans isomeric mixture of the 5-(6-isopropoxy-4-methylmethyl-3-hexenyloxy)-1,3-benzodioxol is obtained as colourless oil. $n_D^{20}=1.5111$.

Analysis: $C_{17}H_{24}O_4$ (molecular weight: 292.4). Calc.: C, 69.8%; H, 8.3%; O, 21.9%. Found: C, 68.9%; H, 8.5%; O, 22.7%.

EXAMPLE 38

4'-(5-Isopropoxy-2-pentenylthio)-acetophenone (according to process (a))

3.4 g. (0.06 mol) of pulverised potassium hydroxide are added to a solution of 8.2 g. (0.06 mol) of p-hydroxy-acetophenone and 14.6 g. (0.09 mol) of 1-chloro-5-isopro-

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poxy-2-pentene in 100 cc. of 1,2-dimethoxyethane. The mixture is stirred at 60° during the course of 24 hours and is subsequently filtered. The filtrate is evaporated at reduced pressure, the residue is taken up in ether, and the ether solution is washed with saturated salt solution. The organic phase is dried with sodium sulphate and evaporated. The residue is chromatographed with hexane/ethyl acetate 4:1 on silica gel and then the 4'-(5-isopropoxy-2-pentenylthio)-acetophenone is obtained as colourless oil. $n_D^{20}=1.5240$.

Analysis: $C_{16}H_{22}O_3$ (molecular weight: 262.3). Calc.: C, 73.3%; H, 8.5%; O, 18.3%. Found: C, 73.3%; H, 8.6%; O, 18.2%.

In analogous manner as described in Example 38, but using 3,4-methylenedioxy-phenol in the place of p-hydroxy-acetophenone, the following compound of general formula I is produced:

EXAMPLE 39

5-(5-Isopropoxy-2-pentenylthio)-1,3-benzodioxol

$n_D^{20}=1.5157$.

Analysis: $C_{15}H_{20}O_4$ (molecular weight: 264.3). Calc.: C, 68.2%; H, 7.6%; O, 24.2%. Found: C, 68.4%; H, 8.0%; O, 24.1%.

EXAMPLE 40

4-[(5-Isopropoxy-2-pentenylthio)-methyl]-chorobenzol (according to process (a))

8.1 g. (0.05 mol) of 1-chloro-5-isopropoxy-2-pentene are added dropwise at 20–25° during the course of 10 minutes and while stirring to a solution of 7.9 g. (0.05 mol) of 4-chloro-benzylmercaptan and 5.6 g. (0.05 mol) of potassium tert.butoxide in 150 cc. of tert.butanol. The solution which is rendered turbid during the addition is stirred at 60° during the course of 1 hour and is then cooled and filtered. The solvent is distilled off at a reduced pressure, the residue is dissolved in ether and the ether solution is washed with saturated salt solution. The ether phase is dried with sodium sulphate and then the ether is distilled off and the residue is chromatographed on silica gel with chloroform. The 4-[(5-isopropoxy-2-pentenylthio)-methyl]-chlorobenzol is obtained as colourless oil having a B.P. of 110–112°/5.10⁻⁴ mm. $n_D^{20}=1.5391$.

Analysis: $C_{15}H_{21}ClOS$ (molecular weight: 284.8). Calc.: C, 63.3%; H, 7.4%; Cl, 12.4%; S, 11.3%. Found: C, 63.2%; H, 7.4%; Cl, 12.7%; S, 11.5%.

EXAMPLE 41

5-[(5-Isopropoxy-3-methyl-2-pentenylthio)-methyl]1,3-benzodioxol (according to process (a))

15.8 g. (0.1 mol) of 5-isopropoxy-3-methyl-1-penten-3-ol are added dropwise at 5° during the course of 15 minutes and while stirring to 40 cc. of 48% hydrobromic acid. After 30 minutes at 0–5° the mixture is extracted with ether, the ether extract is extracted with 10% soda solution and subsequently with saturated salt solution, is dried with sodium sulphate and evaporated.

The obtained 1-bromo-5-isopropoxy-5-methyl-2-pentene (19.0 g.) is added to 17.4 g. (0.1 mol) of sodium salt of 3,4-methylenedioxy-benzyl alcohol in 150 cc. of dimethylformamide and the mixture is stirred at 60° for 5 hours. The reaction mixture is poured on 300 cc. of water and extracted with ether. The ether solution is washed with water, dried with sodium sulphate and evaporated. The residue is chromatographed on silica gel with hexane/ethyl acetate 9:1. A mixture of cis and trans-5-[(5-isopropoxy-3-methyl-2-pentenylthio)-methyl]-1,3-benzodioxol is obtained as colourless oil. $n_D^{20}=1.5088$.

Analysis: $C_{17}H_{24}O_4$ (molecular weight: 292.4). Calc.: C, 69.8%; H, 8.3%. Found: C, 69.4%; H, 8.2%.

In analogous manner as described in Example 41, but using 5-ethoxy-3,5-dimethyl-1-hexen-3-ol in the place of 5-isopropoxy-3-methyl-1-penten-3-ol, the following compound of general formula I is produced.

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EXAMPLE 42

5-[(5-Ethoxy-3,5-dimethyl-2-hexenyloxy)-methyl]1,3-benzodioxol

$n_D^{20}=1.5038$.

Analysis: $C_{18}H_{26}O_4$ (molecular weight: 306.4). Calc.: C, 70.6%; H, 8.6%. Found: C, 70.6%; H, 9.2%.

EXAMPLE 43

5-[(5-Isopropoxy-3-methyl-2-pentenylthio)-methyl]-1,3-benzodioxol (according to process (a))

8.0 g. (0.2 mol) of sodium hydroxide are added to a solution of 30.4 g. (0.2 mol) of 3,4-methylenedioxy-benzyl-alcohol in 300 cc. of benzene. The mixture is heated while stirring vigorously and kept at reflux temperature whereby the water condensing in a refrigerator is separated by means of a water separator. After 24 hours 35.3 g. (0.2 mol) of 1-chloro-5-isopropoxy-3-methyl-2-pentene are added dropwise during the course of 1 hour and the mixture is stirred under reflux for a further 16 hours.

The reaction mixture is cooled and then washed with saturated salt solution, the benzene solution is dried with sodium sulphate, is dried and evaporated. The residue is fractionated at 10⁻⁴ mm. whereby the cis/trans mixture of 5-[(5-isopropoxy-3-methyl-2-pentenylthio)-methyl]1,3-benzodioxol distills at 126–136°.

The product is identical with the compound produced in accordance with Example 41.

EXAMPLE 44

5-(4-Isobutoxy-3-methyl-2-butenylthio)-1,3-benzodioxol (according to process (b))

1.6 g. (0.0165 mol) of sodium-isobutylate in 75 cc. of isobutanol are added dropwise at 70° during the course of 15 minutes to 4.3 g. (0.015 mol) of 5-(4-bromo-3-methyl-2-butenylthio)-1,3-benzodioxol which is dissolved in 130 cc. of isobutanol. After 3 hours at this temperature the reaction mixture is filtered, the solvent is distilled off at reduced pressure and the residue is dissolved in ether. The ether solution is washed with saturated salt solution, is dried with sodium sulphate and evaporated. The residue is chromatographed on silica gel with chloroform. 5-(4-isobutoxy-3-methyl-2-butenylthio)-1,3-benzodioxol is obtained as colourless oil. $n_D^{20}=1.5158$.

Analysis: $C_{16}H_{22}O_4$ (molecular weight: 278.3). Calc.: C, 69.0%; H, 8.0%; O, 23.0%. Found: C, 68.3%; H, 7.8%; O, 23.5%.

In analogous manner as described in Example 44, but using n. butanol as solvent and sodium-n. butylate in the place of sodium-isobutylate, the following compound of general formula I is produced:

EXAMPLE 45

5-(4-n.butoxy-3-methyl-2-butenylthio)-1,3-benzodioxol

$n_D^{20}=1.5168$.

Analysis: $C_{16}H_{22}O_4$ (molecular weight: 278.3). Calc.: C, 69.0%; H, 8.0%; O, 23.0%. Found: C, 68.6%; H, 8.2%; O, 22.8%.

In analogous manner as described in Example 44, but using 4'-(4-bromo-3-methyl-2-butenylthio)-acetophenone in the place of 5-(4-bromo-3-methyl-2-butenylthio)-1,3-benzodioxol, the following compound of general formula I is produced:

EXAMPLE 46

4'-(4-Isobutoxy-3-methyl-2-butenylthio)-acetophenone

$n_D^{20}=1.5282$.

Analysis: $C_{17}H_{24}O_3$ (molecular weight: 276.4). Calc.: C, 73.8%; H, 8.7%; O, 17.3%. Found: C, 73.4%; H, 9.1%; O, 18.1%.

In analogous manner as described in Example 46, but using the sodium salt of the allyl alcohol and allyl alco-

hol as solvent, the following compound of general formula I is produced.

EXAMPLE 47

4'-(4-Allyloxy-3-methyl-2-butenyloxy)-acetophenone

$n_D^{20}=1.5448$.

Analysis: $C_{16}H_{20}O_3$ (molecular weight: 260.3). Calc.: C, 73.8%; H, 7.7%; O, 18.4%. Found: C, 73.2%; H, 7.8%; O, 19.1%.

In analogous manner as described in Example 44, but using 5-[4-(4-bromo-3-methyl-2-butenyloxy)-methyl]-1,3-benzodioxol in the place of 5-(4-bromo-3-methyl-2-butenyloxy)-1,3-benzodioxol, the following compound of general formula I is produced.

EXAMPLE 48

5-[4-(4-Isobutoxy-3-methyl-2-butenyloxy)-methyl]-1,3-benzodioxol

$n_D^{20}=1.5102$.

Analysis: $C_{17}H_{24}O_4$ (molecular weight: 292.4). Calc.: C, 69.8%; H, 8.3%. Found: C, 69.4%; H, 8.1%.

EXAMPLE 49

4'-(4-Benzylthio-3-methyl-2-butenyloxy)-acetophenone (according to process (b))

14.15 g. (0.05 mol) of 4'-(4-bromo-3-methyl-2-butenyloxy)-acetophenone are added at 10–15° during the course of 1 hour to 7.3 g. (0.05 mol) of sodium salt of benzylmercaptan which is dissolved in 120 cc. of dimethylformamide. The mixture is stirred at 20–25° for 20 hours, is subsequently filtered and the filtrate is evaporated at reduced pressure. The residue is dissolved in ether, is extracted with saturated salt solution and the ether solution is evaporated. The remaining yellowish oil is chromatographed on silica gel with hexane/ethyl acetate 2:1. After recrystallization from ether/hexane the 4'-(4-benzylthio-3-methyl-2-butenyloxy)-acetophenone is obtained as colourless crystals. M.P. 75–76.5°.

Analysis: $C_{20}H_{22}O_2S$ (molecular weight: 326.5). Calc.: C, 73.6%; H, 6.8%; S, 9.8%. Found: C, 73.3%; H, 6.7%; S, 9.7%.

EXAMPLE 50

5-(4-Isobutylthio-3-methyl-2-butenyloxy)-1,3-benzodioxol (according to process (b))

A solution of 4.3 g. (0.015 mol) of 5-(4-bromo-3-methyl-2-butenyloxy)-1,3-benzodioxol in 50 cc. of benzene is added at 25° to 1.7 g. (0.015 mol) of sodium-isobutylthio alcoholate in 30 cc. of benzene. The mixture is kept at reflux temperature for 13 hours, is subsequently filtered, washed with saturated salt solution and evaporated. The remaining yellow oil is chromatographed with hexane/ethyl acetate 7:1 on silica gel, whereby colourless 5-(4-isobutylthio-3-methyl-2-butenyloxy)-1,3-benzodioxol is obtained. $n_D^{20}=1.5463$.

Analysis: $C_{16}H_{22}O_3S$ (molecular weight: 294.4). Calc.: C, 65.3%; H, 7.5%; S, 10.9%. Found: C, 65.1%; H, 7.6%; S, 10.6%.

In analogous manner as described in Example 50 the following compound of general formula I is produced, whereby in the place of 5-(4-bromo-3-methyl-2-butenyloxy)-1,3-benzodioxol 4-(4-bromo-3-methyl-2-butenyloxy)-benzoic methyl ester is used.

EXAMPLE 51

4-(4-Isobutylthio-3-methyl-2-butenyloxy)-benzoic methyl ester

$n_D^{20}=1.5428$.

Analysis: $C_{17}H_{24}O_3S$ (molecular weight: 308.4). Calc.: C, 66.2%; H, 7.8%; S, 10.4%. Found: C, 65.2%; H, 7.8%; S, 9.8%.

EXAMPLE 52

4-(4-Isobutoxy-3-methyl-2-butenyloxy)-benzoic methyl ester (according to process (b))

A solution of 6.0 (0.02 mol) of 4-(4-bromo-3-methyl-2-butenyloxy)-benzoic methyl ester and 2.9 g. (0.03 mol) of sodium-isobutylate in 130 g. of isobutanol is stirred at 70° for 6 hours. After this period the reaction mixture is filtered, the filtrate is evaporated at reduced pressure. The residue is dissolved in ether, the ether solution is washed with saturated salt solution, dried with sodium sulphate and evaporated. The residue (6.5 g.) is dissolved in 50 cc. of absolute methanol, 0.54 g. (0.01) mol of sodium methylate is added and the mixture is boiled under reflux for 2 hours. After this period 40 cc. of methanol are distilled off. The remaining residue is dissolved in 100 cc. of ether, the ether solution is extracted twice with 100 cc. amounts of saturated salt solution and dried with sodium sulphate. The ether is distilled off and the resulting 4-(4-isobutoxy-3-methyl-2-butenyloxy)-benzoic methyl ester is purified by chromatography on silica gel with hexane/ethyl acetate 20:1. $n_D^{20}=1.5151$.

Analysis: $C_{17}H_{24}O_4$ (molecular weight: 292.4). Calc.: C, 69.8%; H, 8.3%; O, 21.9%. Found: C, 70.0%; H, 8.4%; O, 22.1%.

EXAMPLE 53

5-(4-Isobutoxy-2-butenyloxy)-1,3-benzodioxol (according to process (b))

1.9 g. (0.02 mol) of sodium-isobutylate in 30 cc. of isobutanol are added dropwise at 50° during the course of 2 hours to a solution of 5.4 g. (0.02 mol) of 5-(4-bromo-2-butenyloxy)-1,3-benzodioxol in 100 cc. of isobutanol. After stirring the reaction mixture at 50° for 6 hours it is filtered and the solvent of the filtrate is distilled off at reduced pressure. The remaining oil is dissolved in ether, the ether solution is extracted with water, dried with sodium sulphate and evaporated. The residue is chromatographed with hexane/ethyl acetate 12:1 on silica gel, whereby the 5-(4-isobutoxy-2-butenyloxy)-1,3-benzodioxol is obtained as colourless oil. $n_D^{20}=1.5102$.

Analysis: $C_{15}H_{20}O_4$ (molecular weight: 264.3). Calc.: C, 68.2%; H, 7.6%. Found: C, 67.4%; H, 7.5%.

The following compound is produced in manner analogous to that described in Example 53, but using 4'-(4-bromo-2-butenyloxy)-acetophenone in the place of 5-(4-bromo-2-butenyloxy)-1,3-benzodioxol.

EXAMPLE 54

4'-(4-Isobutoxy-2-butenyloxy)-acetophenone

$n_D^{20}=1.5262$.

Analysis: $C_{16}H_{22}O_3$ (molecular weight: 262.3). Calc.: C, 73.3%; H, 8.5%. Found: C, 73.5%; H, 8.6%.

In manner analogous to that described in Example 53 the following compound is produced, whereby 5-[4-(4-bromo-2-butenyloxy)-methyl]-1,3-benzodioxol is used in the place of 5-(4-bromo-2-butenyloxy)-1,3-benzodioxol:

EXAMPLE 55

5-[4-(4-Isobutoxy-2-butenyloxy)-methyl]-1,3-benzodioxol

$n_D^{20}=1.5110$.

Analysis: $C_{16}H_{22}O_4$ (molecular weight: 278.3). Calc.: C, 69.0%; H, 8.0%. Found: C, 68.7%; H, 7.9%.

EXAMPLE 56

5-(7-Isopropoxy-5-methyl-4-heptenyloxy)-1,3-benzodioxol (according to process (c))

A mixture of 2.5 g. (0.013 mol) of 7-isopropoxy-5-methyl-4-cis,trans-heptenol, 1.25 g. (0.009 mol) of 3,4-

methylendioxy-phenol, and 2.22 g. (0.011 mol) of dicyclohexyl carbodiimide are stirred at 100° for 18 hours. After cooling the residue is chromatographed with hexane/ethyl acetate 99:1 on silica gel. A cis,trans mixture of 5-(7-isopropoxy-5-methyl-4-heptenyloxy)-1,3-benzodioxol is obtained. $n_D^{20}=1.5017$.

Analysis: $C_{18}H_{26}O_4$ (molecular weight: 306.4). Calc.: C, 70.6%; H, 8.6%. Found: C, 70.8%; H, 8.8%.

EXAMPLE 57

5-(5-Isopropoxy-2-pentenylthio)-1,3-benzodioxol (according to process (c))

A mixture of 7.2 g. (0.05 mol) of 5-isopropoxy-2-penten-1-ol, 6.9 g. (0.05 mol) of 3,4-methylendioxy-phenol, and 10.3 g. (0.05 mol) of dicyclohexyl-carbodiimide is stirred at 105° for 16 hours. After cooling 50 cc. of ether are added, the mixture is filtered and the filtrate is evaporated. The residue is chromatographed on silica gel with hexane/ethyl acetate 9:1 and 5-(5-isopropoxy-2-pentenylthio)-1,3-benzodioxol is obtained as colourless oil which is identical with the product produced in accordance with Example 39.

EXAMPLE 58

4-[(5-Isopropoxy-2-pentenylthio)-methyl]-chlorobenzol (according to process (d))

A solution of 8.0 g. (0.05 mol) of 5-isopropoxy-2-penten-1-thiol and 2 g. (0.05 mol) of sodium hydroxide in 30 cc. of ethanol are added dropwise at 50° during the course of 45 minutes to a solution of 8.05 g. (0.05 mol) of p-chloro-benzylchloride in 25 cc. of ethanol, the temperature not exceeding 55°. After the addition is complete the mixture is heated to 60° during 10 minutes. The reaction mixture is filtered, the ethanol is distilled off and the residue is chromatographed on silica gel with chloroform, whereby 4-[(5-isopropoxy-2-pentenylthio)-methyl]-chlorobenzol is obtained which is identical with the compound produced in accordance with Example 40.

EXAMPLE 59

5-[(5-Isopropoxy-3-methyl-2-pentenylthio)-methyl]-1,3-benzodioxol (according to process (d))

3.16 g. (0.02 mol) of 5-isopropoxy-3-methyl-2-penten-1-ol are added at room temperature to a solution of 1.36 g. (0.02 mol) of sodium ethylate in 30 cc. of ethanol. The solvent is distilled off at reduced pressure and the residue which is dried well at room temperature is dissolved in 30 cc. of dimethylsulphoxide. 4.3 g. (0.02 mol) of 3,4-methylenedioxy-benzylbromide (produced according to P. Karrer et al., *Helv. Chim. Acta*, 6, 905 [1923]) which are dissolved in 20 cc. of dimethylsulphoxide are added dropwise at 0° to this solution. The mixture is stirred at room temperature for 2 hours and subsequently at 60° for 18 hours.

The reaction mixture is poured on 200 cc. of water, is extracted with ether and the ether extract is washed with saturated salt solution. After the drying of the ether extract with sodium sulphate and distillation of the solvent the residue is chromatographed on silica gel with hexane/ethyl acetate 9:1. The resulting cis/trans isomeric mixture of 5-[(5-isopropoxy-3-methyl-2-pentenylthio)-methyl]-1,3-benzodioxol is identical with the isomeric mixture produced in accordance with Example 41.

EXAMPLE 60

1,4-Bis(1-benzodioxol-5-yloxy)-2-methyl-2-butene

3.2 g. (0.02 mol) of sodium salt of 3,4-methyendioxy-phenol are suspended in 60 cc. of 1,2-dimethoxyethane

and cooled to 0-5°. 2.28 g. (0.01 mol) of 1,4-bromo-2-methyl-2-butene, dissolved in 20 cc. of 1,2-dimethoxyethane are added while stirring. The mixture is stirred at 20-25° during the course of 20 hours and 50° during the course of 5 hours; it is subsequently filtered and the filtrate is evaporated. The residue is taken up in ether, extracted with saturated salt solution, the ether phase is dried with sodium sulphate and evaporated. The obtained viscous oil is purified by chromatography on silica gel with hexane/ethyl acetate 5:1 and subsequently by crystallization from ethyl acetate/hexane. M.P. 73.5-74°.

Analysis: $C_{18}H_{18}O_6$ (molecular weight: 342.3). Calc.: C, 66.7%; H, 5.3%. Found: C, 66.7%; H, 5.6%.

In analogous manner as described in Example 60, but using sodium salt of 4-hydroxy-benzoic methyl ester in the place of the sodium salt of 3,4-methyendioxy-phenol, the following compound is produced.

EXAMPLE 61

4,4'-(2-Methyl-2-buten-1,4-ylendioxy)-bis(benzoic methyl ester)

M.P. 134-135°.

Analysis: $C_{21}H_{22}O_8$ (molecular weight: 370.4). Calc.: C, 68.1%; H, 6.0%; O, 25.9%. Found: C, 68.6%; H, 6.2%; O, 25.5%.

In analogous manner as described in Example 60, but using the sodium salt of 3,4-methyendioxy-benzylalcohol in the place of the sodium salt of 3,4-methyendioxy-phenol, the following compound is produced.

EXAMPLE 62

1,4-Bis(piperonyloxy)-2-methyl-2-butene

$n_D^{20}=1.5537$.

Analysis: $C_{21}H_{22}O_6$ (molecular weight: 370.4). Calc.: C, 68.1%; H, 6.0%. Found: C, 68.0%; H, 6.5%.

The alcohols of general formula VIII required for the production of the compounds of formula I without isolation of the compounds of general formula II may be produced with the following Example:

EXAMPLE 63

5-Isopropoxy-3-methyl-1-penten-3-ol

12 g. (0.5 mol) of magnesium cuttings are covered with a layer of 60 cc. of absolute tetrahydrofuran in an atmosphere of nitrogen in a flask equipped with a stirrer and a reflux condenser cooled with ice, and are heated to 40-45°. 5 cc. of a solution of 53.5 g. (0.5 mol) of vinyl bromide in 100 cc. of absolute tetrahydrofuran are added dropwise by means of a dropping funnel, whereupon an exothermic reaction sets in. The remaining vinyl bromide solution is added dropwise at such a rate that the reaction mixture maintains a temperature of 45° to 50° (approximately 1 to 1½ hours). Then the mixture is stirred at 50° for 1 hour and subsequently cooled to 0°. 52 g. (0.4 mol) of 4-isopropoxy-2-butanone in 100 cc. of absolute tetrahydrofuran are added dropwise during the course of 45 minutes and while stirring vigorously; the reaction mixture is subsequently stirred at room temperature during the course of 16 hours. After this period 250 cc. of a 20% ammonium chloride solution are added during the course of 15 minutes to the reaction mixture which is cooled to 5-10°. The mixture is stirred for 15 minutes and extracted with ether. The ether extract is washed with water in a separatory funnel, is dried with sodium sulphate and evaporated. The residue is fractionated at 13 mm. pressure, whereby the 5-isopropoxy-3-methyl-1-penten-3-ol distils at 72-73°. n_D^{20} : 1.4297.

Analysis: $C_9H_{18}O_2$ (molecular weight: 158.2). Calc.: C, 68.3%; H, 11.5%. Found: C, 68.1%; H, 11.4%.

Exam- ple		Empirical formula	Molec- ular weight	B.P./mm.	n_D^{20}	Analysis percent, calc./found			Starting compound of formula IX
						C	H	S	
64.....	3-ethyl-5-isopropoxy-1-penten-3-ol.....	C ₁₀ H ₂₀ O ₂	172.3	81-84°/12	1.4346	69.7 69.4	11.7 11.5	-----	1-isopropoxy-3-pentanone.
65.....	5-sec.butoxy-3-methyl-1-penten-3-ol.....	C ₁₀ H ₂₀ O ₂	172.3	87-91°/15	1.4352	69.7 69.6	11.7 11.6	-----	4-sec.butoxy-2-butanone.
66.....	3-ethyl-5-sec.butoxy-1-penten-3-ol.....	C ₁₁ H ₂₂ O ₂	186.3	113-15°/30	1.4380	70.9 71.2	11.9 11.8	-----	1-sec.butoxy-3-pentanone.
67.....	5-tert.butoxy-3-methyl-1-penten-3-ol.....	C ₁₀ H ₂₀ O ₂	172.3	78-81°/12	1.4316	69.7 69.2	11.7 11.4	-----	4-tert.butoxy-2-butanone.
68.....	5-isopropylthio-3-methyl-1-penten-3-ol.....	C ₉ H ₁₈ OS	174.3	79-80°/1.2	1.4813	62.0 61.5	10.4 10.4	18.4 18.9	4-isopropylthio-2-butanone.
69.....	5-sec.butylthio-3-methyl-1-penten-3-ol.....	C ₁₀ H ₂₀ OS	188.3	86-89°/0.85	1.4844	63.8 63.3	10.7 10.5	17.0 17.4	4-sec.butylthio-2-butanone.
70.....	5-cyclohexyloxy-3-methyl-1-penten-3-ol.....	C ₁₂ H ₂₂ O ₂	198.3	87-90°/0.6	1.4669	72.7 72.8	11.2 11.6	-----	4-cyclohexyloxy-2-butanone.
71.....	5-cyclopentyloxy-3-methyl-1-penten-3-ol.....	C ₁₁ H ₂₀ O ₂	184.3	76-79°/1.2	1.4612	71.7 71.6	10.9 11.0	-----	4-cyclopentyloxy-2-butanone.
72.....	3-methyl-5-(2-pentyloxy)-1-penten-3-ol.....	C ₁₁ H ₂₂ O ₂	186.3	64-67°/1.0	1.4358	70.9 70.4	11.9 12.2	-----	4-(2-pentyloxy)-2-butanone.
73.....	3-methyl-5-(3-pentyloxy)-1-penten-3-ol.....	C ₁₁ H ₂₂ O ₂	186.3	66-69°/1.0	1.4377	70.9 70.3	11.9 11.8	-----	4-(3-pentyloxy)-2-butanone.
74.....	5-n.butoxy-3-methyl-1-penten-3-ol.....	C ₁₀ H ₂₀ O ₂	172.3	115-19°/33	1.4370	69.7 69.3	11.7 11.5	-----	4-n.butoxy-2-butanone.
75.....	5-ethoxy-3-methyl-1-penten-3-ol.....	C ₈ H ₁₆ O ₂	144.2	90-92°/46	1.4325	66.6 66.9	11.2 11.0	-----	4-ethoxy-2-butanone.
76.....	5-ethoxy-3,5-dimethyl-1-hexen-3-ol.....	C ₁₀ H ₂₀ O ₂	172.3	87-89°/16	1.4383	69.7 69.3	11.7 11.6	-----	4-ethoxy-4-methyl-2-pentanone.*
77.....	3-methyl-5-(6-methyl-5-hepten-2-yloxy)-1-penten-3-ol.	C ₁₄ H ₂₆ O ₂	226.4	-----	1.4627	74.3 74.0	11.6 11.5	-----	4-(6-methyl-5-hepten-2-yloxy)-2-butanone.

*Produced in accordance with A. Hoffman, J. Amer. Chem. Soc. 49, 532 [1927];

The compounds of general formula II may be produced in accordance with the following Example:

EXAMPLE 78

6-Ethoxy-1-bromo-3-methyl-2-hexene

3.9 g. (0.03 mol) of 5-ethoxy-2-pentanone (produced in accordance with A. H. Tracy et al., J. Org. Chem., 6, 68 [1941]) in 10 cc. of tetrahydrofuran are added dropwise at 0° during the course of 30 minutes and while stirring to the Grignard reagent, produced from 0.96 g. (0.04 mol) of magnesium and 4.3 g. (0.04 mol) of vinyl bromide in 20 cc. of tetrahydrofuran. After stirring at 20-25° for 15 hours the mixture is cooled to 5-10°; 25 cc. of 20% ammonium chloride solution are added and after 10 minutes it is extracted with ether. The ether extract is washed with saturated salt solution, dried with sodium sulphate and evaporated. The residue which is uniform in accordance with gas-chromatography (4.5 g. of 6-ethoxy-3-methyl-1-hexen-3-ol) is added at 0° during the course of 5 minutes to 12 cc. of 48% hydrobromic acid. The mixture is stirred at 0-5° during the course of 30 minutes and then the ether is extracted, the ether solution is washed with saturated salt solution, dried with sodium sulphate and evaporated. The resulting 6-ethoxy-1-bromo-3-methyl-2-hexene is used without purification.

EXAMPLE 79

1-Bromo-4-isobutoxy-2-methyl-2-butene

6.8 g. (0.03 mol) of 1,4-dibromo-2-methyl-2-butene are dissolved in 15 cc. of isobutanol and 2.9 g. (0.03 mol) of sodium isobutylate in 50 cc. of isobutanol are added at 0°. After stirring at 0° for 2 hours the mixture is stirred at 20-25° for 16 hours. The mixture is filtered and the filtrate is evaporated at reduced pressure. The residue is dissolved in ether, washed with saturated salt solution and dried with sodium sulphate. The ether is evaporated and the residue is distilled at 13 mm. The product has a B.P. of 128-138°/13 mm.

Analysis: C₉H₁₇BrO (molecular weight: 221.1). Calc.: C, 48.9%; H, 7.7%; Br, 36.1%. Found: C, 49.0%; H, 7.8%; Br, 35.6%.

The compounds of general formula II via formula XIV may be produced in accordance with the following Example:

EXAMPLE 80

1-Bromo-6-isopropoxy-4-methyl-3-hexene

A solution of 46 g. (0.35 mol) of 4-isopropoxy-2-butanone in 100 cc. of absolute tetrahydrofuran is added dropwise at 5° during the course of 10 minutes in an atmosphere of nitrogen and while stirring to the Grignard reagent (according to E. Renk et al., J. Amer. Chem. Soc., 83, 1987 [1961]) produced from 9.06 g. (0.38 mol) of magnesium and 42.8 g. (0.35 mol) of cyclopropyl bromide in 460 cc. of absolute tetrahydrofuran. After stirring the reaction mixture at room temperature for 20 hours saturated ammonium chloride solution and ice are added and the mixture is extracted with ether. The ether extract is washed with saturated salt solution, dried over sodium sulphate and evaporated. The resulting 2-cyclopropyl-4-isopropoxy-2-butanone, having a B.P. of 75-77°/12 mm., may be worked up without purification.

19 cc. of 48% hydrobromic acid are added dropwise at 0° during the course of 15 minutes and while stirring to 27.7 g. of crude product. The mixture is stirred at 0-5° during the course of 30 minutes and subsequently extracted with ether. The ether extract is washed with water, saturated sodium bicarbonate, and saturated salt solution, dried over sodium sulphate and evaporated. The residue (20.2 g.) is chromatographed with hexane/ethyl acetate 98:2 and 95:5 on 1 kg. of silica gel. A chromatographically uniform cis/trans isomeric mixture of 1-bromo-6-isopropoxy-4-methyl-3-hexene is thus obtained. $n_D^{20}=1.4721$.

Analysis: C₁₀H₁₉BrO (molecular weight: 235.2). Calc.: C, 51.1%; H, 8.1%; Br, 34.0%; O, 6.8%. Found: C, 50.8%; H, 8.0%; Br, 34.2%; O, 7.0%.

The compounds of formula IX required for the production of the compounds of formulae VIII and XIV may, for example, be produced in accordance with the following Example:

EXAMPLE 81

4-Isopropoxy-2-butanone

0.3 g. of concentrated sulphuric acid are added to 7.2 g. (0.12 mol) of isopropanol. A mixture of 21 g. (0.3 mol) of vinyl methyl ketone and 36 g. (0.6 mol) of isopropanol is added dropwise at room temperature during the course of 1 hour and while stirring, the temperature not exceeding 30°. After 24 hours 1.6 g. of potassium carbonate and 2 drops of water are added at room temperature, the mixture is stirred vigorously for 2 hours and filtered; the clear filtrate which now reacts neutrally is fractionated at 36 mm. The excess of isopropanol distills and then the 4-isopropoxy-2-butanone at 73–76°/36 mm.

Analysis: $C_8H_{14}O_2$ (molecular weight: 130.2). Calc.: C, 64.6%; H, 10.8%. Found: C, 64.1%; H, 10.8%.

In analogous manner as described in Example 81, but using 6-methyl-5-hepten-2-ol in the place of isopropanol, the following compound is used.

EXAMPLE 82

4-(6-Methyl-5-hepten-2-yloxy)-2-butanone

B.P. 82–85°/1.0 mm.

$n_D^{20}=1.4462$.

Analysis: $C_{12}H_{22}O_2$ (molecular weight: 198.3). Calc.: C, 72.7%; H, 11.2%. Found: C, 71.8%; H, 11.1%.

The compounds of general formula II, wherein Y signifies oxygen and Hal signifies chlorine, may, for example, be produced as follows:

EXAMPLE 83

1-Chloro-5-isopropoxy-3-methyl-2-pentene

32.4 g. of chloromethyl-isopropylether are added dropwise at 0° during the course of 40 minutes and while stirring to 20.4 g. (0.3 mol) of isoprene and 0.3 g. of zinc chloride. The mixture is then stirred at room temperature for 24 hours. The reaction mixture is taken up in ether, is washed with water and subsequently with sodium bicarbonate solution and again with water. The ether phase is dried with sodium sulphate, the ether is distilled off and the residue is distilled at 12 mm., whereby 1-chloro-5-isopropoxy-3-methyl-2-pentene is obtained as colourless oil. B.P. 86–92°/12 mm., $n_D^{20}=1.4553$.

Analysis: $C_9H_{17}ClO$ (molecular weight: 176.7). Calc.: C, 61.2%; H, 9.7%; Cl, 20.1%. Found: C, 61.3%; H, 9.6%; Cl, 20.3%.

EXAMPLE 84

1-Chloro-5-isopropoxy-2-pentene

13 g. (0.24 mol) of butadiene are introduced at 10–15° during the course of 1½ hours and while stirring into a suspension of 0.8 g. of newly melted zinc chloride in 21.7 g. (0.2 mol) of chloromethyl-isopropylether. The mixture which has now turned yellow is stirred at 10° for 1 hour. After this period 20 cc. of 10% sodium carbonate solution are added dropwise, 100 cc. of benzene are added and the aqueous phase is separated in a separatory funnel. The benzene solution is washed with 10% sodium carbonate solution and subsequently with water, is dried with magnesium sulphate and evaporated at reduced pressure. The residue is distilled at 90 mm. B.P. of 1-chloro-5-isopropoxy-2-pentene: 110–112°/90 mm. $n_D^{20}=1.4408$.

Analysis: $C_8H_{15}ClO$ (molecular weight: 162.7). Calc.: C, 59.1%; H, 9.3%; Cl, 21.8%. Found: C, 59.2%; H, 9.3%; Cl, 21.1%.

The compounds of general formula IV may be produced in accordance with the following Example:

EXAMPLE 85

5-(4-Bromo-3-methyl-2-butenyloxy)-1,3-benzodioxol

25.1 g. (0.11 mol) of 1,4-dibromo-2-methyl-2-butene are dissolved in 120 cc. of 1,2-dimethoxyethane and cooled to –20°. 16.0 g. (0.1 mol) of sodium salt of the 3,4-methylenedioxy-phenol in 170 cc. of 1,2-dimethoxyethane are added during the course of 15 minutes to this solution. After stirring at 0° for 1 hour and at 20° for 15 minutes the solvent is distilled off in a vacuum. The residue is dissolved in ether, is washed with saturated salt solution and dried with sodium sulphate. The ether is evaporated and an oily residue remains which is purified by chromatography on silica gel with hexane/ethyl acetate 9:1.

Analysis: $C_{12}H_{13}BrO_3$ (molecular weight: 285.1). Calc.: C, 50.5%; H, 4.6%; Br, 28.0%; O, 16.8%. Found: C, 50.4%; H, 4.5%; Br, 28.3%; O, 17.0%.

In analogous manner as described in Example 85, but using the sodium salt of p-hydroxy-acetophenone in the place of the sodium salt of 3,4-methylenedioxy-phenol, the following compound of general formula IV is produced:

EXAMPLE 86

4'-(4-Bromo-3-methyl-2-butenyloxy)-acetophenone

Analysis: $C_{13}H_{15}BrO_2$ (molecular weight: 283.2). Calc.: C, 55.1%; H, 5.3%; Br, 28.2%. Found: C, 54.7%; H, 5.3%; Br, 28.5%.

In analogous manner as described in Example 85, but using the sodium salt of the 4-hydroxy-benzoic methyl ester in the place of the sodium salt of 3,4-methylenedioxy-phenol, the following compound is produced.

EXAMPLE 87

4-(4-Bromo-3-methyl-2-butenyloxy)-benzoic methyl ester

M.P. 50–52°.

Analysis: $C_{13}H_{15}BrO_3$ (molecular weight: 299.2). Calc.: C, 52.2%; H, 5.1%; Br, 26.7%. Found: C, 52.3%; H, 5.1%; Br, 26.4%.

EXAMPLE 88

5-[(4-Bromo-3-methyl-2-butenyloxy)-methyl]-1,3-benzodioxol

8.7 g. (0.05 mol) of sodium salt of the 3,4-methylenedioxybenzylalcohol are added at 0° during the course of 15 minutes and while stirring to 12.5 g. (0.055 mol) of 1,4-dibromo-2-methyl-2-butene which is dissolved in 100 cc. of 1,2-dimethoxyethane. The mixture is stirred at 20–25° for 16 hours and at 50° for 15 minutes. The solvent is then distilled off at reduced pressure and 100 cc. amounts of water and ether are added to the residue. The aqueous phase is separated in a separatory funnel, the ether phase is extracted with saturated salt solution, is dried and sodium sulphate and evaporated. The residue is chromatographed on silica gel with hexane/ethyl acetate 9:1, whereby the 5-[(4-bromo-3-methyl-2-butenyloxy)-methyl]-1,3-benzodioxol is obtained as uniform colourless oil.

Analysis: $C_{13}H_{15}BrO_3$ (molecular weight: 299.2). Calc.: C, 52.2%; H, 5.1%; Br, 26.7%. Found: C, 51.8%; H, 5.0%; Br, 27.6%.

EXAMPLE 89

5-(4-Bromo-2-butenyloxy)-1,3-benzodioxol

6.4 g. (0.04 mol) of sodium salt of 3,4-methylenedioxy-phenol are added at –20° to a solution of 8.6 g. (0.04 mol) of 1,4-dibromo-2-butene in 100 cc. of 1,2-dimethoxyethane. The mixture is stirred at 0° for 3 hours and subsequently at room temperature for 1 hour. The solvent is distilled off at reduced pressure and the residue is taken up in ether. The ether solution is extracted with saturated salt solution, is dried with sodium sulphate and evaporated.

The residue is purified by chromatography on silica gel with hexane/ethyl acetate 9:1. The 5-(4-bromo-2-butenyloxy)-1,3-benzodioxol is obtained as colourless oil.

Analysis: $C_{11}H_{11}BrO_3$ (molecular weight: 271.1). Calc.: C, 48.7%; H, 4.1%; Br, 29.5%. Found: C, 48.6%; H, 4.2%; Br, 29.9%.

In analogous manner as described in Example 89, but using the sodium salt of p-hydroxy-acetophenone in the place of the sodium salt of 3,4-methylenedioxy-phenol, the following compound is produced:

EXAMPLE 90

4'-(4-Bromo-2-butenyloxy)-acetophenone

Analysis: $C_{12}H_{13}BrO_2$ (molecular weight: 269.1). Calc.: C, 53.6%; H, 4.9%; Br, 29.7%. Found: C, 53.9%; H, 5.1%; Br, 30.7%.

EXAMPLE 91

5-[(4-Bromo-2-butenyloxy)-methyl]-1,3-benzodioxol

11.8 g. (0.055 mol) of 1,4-dibromo-2-butene and 8.7 g. (0.05 mol) of sodium salt of 3,4-methylenedioxy-benzyl-alcohol are covered with a layer of 100 cc. of 1,2-dimethoxyethane. The mixture is stirred at 20–25° for 16 hours and at 50° for 15 minutes. The solvent is subsequently distilled off at reduced pressure, the residue is taken up in ether and the ether solution is extracted with water. The organic phase is dried with sodium sulphate and the ether is then distilled off and the residue is chromatographed on silica gel with hexane/ethyl acetate 9:1. The chromatographically uniform 5-[(4-bromo-2-butenyloxy)-methyl]-1,3-benzodioxol is obtained as slightly yellow oil.

Analysis: $C_{12}H_{13}BrO_3$ (molecular weight: 285.1). Calc.: C, 50.5%; H, 4.6%; Br, 28.0%. Found: C, 50.4%; H, 4.7%; Br, 27.5%.

The compounds of general formula VI may be produced in accordance with the following Example:

EXAMPLE 92

7-Isopropoxy-5-methyl-4-heptenal

A solution of 3.68 g. (0.02 mol) of 7-isopropoxy-5-methyl-4-cis,trans-heptenal in 6.5 cc. of ethanol is added dropwise at 0–5° during the course of 10 minutes and while stirring to a mixture of 0.76 g. (0.02 mol) of sodium borohydride, 40 cc. of water, 4 drops of 2N sodium hydroxide, and 40 cc. of ethanol. After stirring for 2 hours at room temperature 60 cc. of water are added to the reaction mixture which is concentrated by evaporation in a vacuum and extracted with ether after saturation with common salt. The ether extract is washed with water and saturated salt solution, dried over sodium sulphate and evaporated. The residue is chromatographed with hexane/ethyl acetate 9:1 on 180 g. of silica gel, whereby pure 7-isopropoxy-5-methyl-4-cis,trans-heptenal is obtained.

Analysis: $C_{11}H_{22}O_2$ (molecular weight: 186.3). Calc.: C, 70.9%; H, 11.9%. Found: C, 70.9%; H, 11.9%.

The compounds of general formula XVI are produced in accordance with the following Example:

EXAMPLE 93

7-Isopropoxy-5-methyl-4-heptenal

15.8 g. (0.1 mol) of 5-isopropoxy-3-methyl-1-penten-3-ol: (produced in accordance with Example 63) and 20.0 g. of mercury acetate are kept in 180 cc. of ethylvinyl ether at reflux temperature during the course of 4 days. 0.9 cc. of glacial acetic acid is added at 20° to the solution which has rendered turbid. 150 cc. of 5% potassium carbonate solution are added after 3 hours and the mixture is extracted with hexane. The hexane extract is evaporated and the residue is heated to 165–168° during 1½ hours in an atmosphere of nitrogen and without further purification; the residue is subsequently distilled at reduced pressure. B.P. of 7-isopropoxy-5-methyl-4-heptenal: 70–73°/0.8 mm. $n_D^{20}=1.4476$.

Analysis: $C_{11}H_{20}O_2$ (molecular weight: 184.3). Calc.: C, 71.7%; H, 10.9%. Found: C, 71.7%; H, 10.8%.

EXAMPLE 94

5-Isopropoxy-2-penten-1-ol

8.13 g. (0.05 mol) of 1-chloro-5-isopropoxy-2-pentene are added to a solution of 6.5 g. of sodium carbonate in 60 cc. of water and the mixture is heated to 95–98° during 18 hours. After cooling the organic parts are extracted with benzene, the benzene extract is washed with saturated salt solution and dried with sodium sulphate. The solvent is distilled off and then it is distilled at reduced pressure. According to gas-chromatography pure 5-isopropoxy-2-penten-1-ol distils at 102–104°/15 mm. $n_D^{20}=1.4363$.

Analysis: $C_8H_{16}O_2$ (molecular weight: 144.2). Calc.: C, 66.6%; H, 11.2%; O, 22.2%. Found: C, 66.4%; H, 11.0%; O, 22.6%.

In analogous manner as described in Example 94 the following compound is produced.

EXAMPLE 95

5-Isopropoxy-3-methyl-2-penten-1-ol

$n_D^{20}=1.4519$.

B.P. 115–118°/15 mm.

Analysis: $C_9H_{18}O_2$ (molecular weight: 158.2). Calc.: C, 68.3%; H, 11.5%; O, 20.2%. Found: C, 67.2%; H, 11.3%; O, 19.3%.

EXAMPLE 96

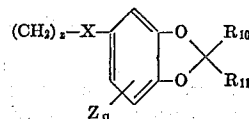
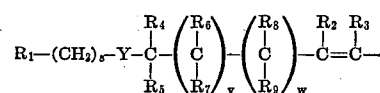
5-Isopropoxy-2-penten-1-thiol

A mixture of 8.1 g. (0.05 mol) of 1-chloro-5-isopropoxy-2-pentene, 3.8 g. (0.05 mol) of thiourea, and 5 cc. of water are heated to 98° during the course of 35 minutes and stirred at this temperature for 30 minutes. The homogeneous reaction mixture is cooled to 60° and 10 cc. (0.05 mol) of 5N caustic soda solution are added dropwise at this temperature. The mixture which again has rendered heterogeneous is heated to 100° with stirring, is cooled after 5 minutes and poured on water. The reaction mixture is extracted with ether, the ether extract is washed with saturated salt solution, is dried with sodium sulphate and the ether is evaporated. The residue is fractionated at 16 mm., whereby the 5-isopropoxy-2-penten-1-thiol is obtained as malodorous oil which is uniform according to gas-chromatography; it has a B.P. of 87–89°/16 mm. $n_D^{20}=1.4696$.

Analysis: $C_8H_{16}SO$ (molecular weight: 160.3). Calc.: C, 60.0%; H, 10.1%; S, 20.0%; O, 10.0%. Found: C, 60.1%; H, 10.1%; S, 18.7%; O, 10.9%.

What is claimed is:

1. A compound of the formula:



stituted by lower acyloxy; and = represents a single wherein

Z is alkyl of 1 to 5 carbon atoms, alkenyl of 2 to 12 carbon atoms, alkoxy of 1 to 5 carbon atoms, alkenyloxy of 2 to 12 carbon atoms, formyl, alkyl carbonyl of 2 to 6 carbon atoms, alkoxy carbonyl of 2 to 6 carbon atoms, mono- or di-alkyl substituted carbamoyl each alkyl substituent of which is of 1 to 5 carbon atoms, alkoxy methylene of 2 to 6 carbon atoms, alkylthio of 1 to 5 carbon atoms, fluorine, chlorine, bromine, cyano or nitro,

R_{10} and R_{11} , which may be the same or different, are each hydrogen or alkyl of 1 to 5 carbon atoms, q is 0 or 1,

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- R_1 is alkyl of 1 to 11 carbon atoms or an acyclic hydrocarbon of up to 11 carbon atoms having one or two double bonds or one triple bond,
 R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , R_8 and R_9 , which may be the same or different, are each hydrogen, alkyl of 1 to 5 carbon atoms or alkenyl of 2 to 6 carbon atoms,
 Y is oxygen or sulphur,
 X is oxygen, sulphur, $-\text{OCH}_2-$ or $-\text{SCH}_2-$,
 s , v and w , which may be the same or different, are each 0 or 1, and
 z is 1, 2 or 3.
2. The compound of Claim 1, which is 5-(3-ethyl-5-sec-butoxy-2-pentenyl-1,3-benzodioxol.
 3. The compound of Claim 1, which is 5-(3-ethyl-5-isopropoxy-2-pentenyl-1,3-benzodioxol.
 4. The compound of Claim 1, which is 5-(5-tert.butoxy-3-methyl-2-pentenyl-1,3-benzodioxol.
 5. The compound of Claim 1, which is 5-(5-isopropylthio-3-methyl-2-pentenyl-1,3-benzodioxol.
 6. The compound of Claim 1, which is 5-[3-methyl-5-(3-pentenyl-2-pentenyl)-1,3-benzodioxol.
 7. The compound of Claim 1, which is 5-[3-methyl-5-(2-pentenyl)-2-pentenyl]-1,3-benzodioxol.
 8. The compound of Claim 1, which is 5-[(5-isopropoxy-3-methyl-2-pentenyl)methyl]-1,3-benzodioxol.
 9. The compound of Claim 1, which is 5-(5-isopropoxy-3-methyl-2-pentenyl)-1,3-benzodioxol.
 10. The compound of Claim 1, which is 5-(5-ethoxy-3-methyl-2-pentenyl)-1,3-benzodioxol.
 11. The compound of Claim 1, which is 5-(5-n.butoxy-3-methyl-2-pentenyl)-1,3-benzodioxol.
 12. The compound of Claim 1, which is 5-(6-ethoxy-3-methyl-2-hexenyl)-1,3-benzodioxol.
 13. The compound of Claim 1, which is 5-(4-isobutoxy-2-methyl-2-butenyl)-1,3-benzodioxol.
 14. The compound of Claim 1, which is 5-(6-isopropoxy-4-methyl-3-hexenyl)-1,3-benzodioxol.
 15. The compound of Claim 1, which is 5-(5-isopropoxy-2-pentenyl)-1,3-benzodioxol.

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16. The compound of Claim 1, which is 5-(4-isobutoxy-3-methyl-2-butenyl)-1,3-benzodioxol.
17. The compound of Claim 1, which is 5-(4-n.butoxy-3-methyl-2-butenyl)-1,3-benzodioxol.
18. The compound of Claim 1, which is 5-[(4 - isobutoxy-3-methyl-2-butenyl)-methyl]-1,3-benzodioxol.
19. The compound of Claim 1, which is 5-(4-isobutylthio-3-methyl-2-butenyl)-1,3-benzodioxol.
20. The compound of Claim 1, which is 5-(4-isobutoxy-2-butenyl)-1,3-benzodioxol.
21. The compound of Claim 1, which is 5-[(4 - isobutoxy-2-butenyl)-methyl]-1,3-benzodioxol.
22. The compound of Claim 1, which is 5-(7 - isopropoxy-5-methyl-4-heptenyl)-1,3-benzodioxol.
23. The compound of Claim 1, which is 5-[3-methyl-5-(6-methyl-5-hepten-2-yl)-2-pentenyl]-1,3 - benzodioxol.
24. The compound of Claim 1, which is 5-[(5-ethoxy-3,5-dimethyl-2-hexenyl)-methyl]-1,3-benzodioxol.

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U.S. Cl. X.R.

260—340.3, 473 R, 592, 609 R, 611 A; 424—282