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2,934,556

BORON COMPOUNDS AND METHODS OF PREPARATION

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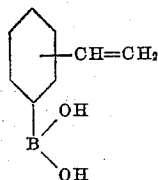
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Serial No. 682,312

22 Claims. (Cl. 260-462)

This invention relates to new chemical compounds and to a method of preparing the same and, more particularly, to new and useful boron compounds and their preparation. Still more particularly the invention is concerned with the production of compounds of the class consisting of the vinylphenyl boronic acids, the vinylphenyl boroxoles and the vinylphenyl boronates.

The vinylphenyl boronic acids of this invention may be represented by the following general formula:

(I)



Compounds embraced by Formula I include the o-, m- and p-vinylphenyl boronic acids, and the term "a vinylphenyl boronic acid" as used generically herein and in the appended claims includes both the pure or substantially pure isomers of vinylphenyl boronic acid, as well as any two or all three of the aforementioned isomers in any proportions.

(The phenyl radical represented, for purpose of simplicity, by the symbol



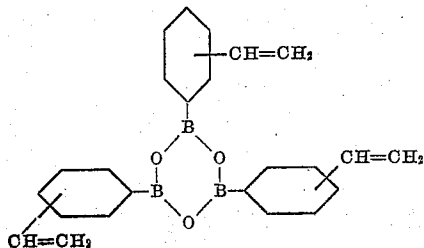
in Formula I and in other formulas that follow [including those in the appended claims] also is frequently represented by the symbol



in order to indicate the aromatic unsaturation; and, hence, the latter symbol could be substituted, if desired, for the symbol used for the phenyl radical in Formula I and other formulas appearing in the specification and claims of this case.)

The vinylphenyl boroxoles of this invention may be represented by the following general formula:

(II)

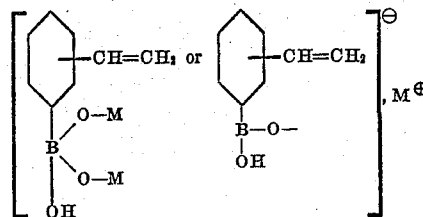


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Compounds embraced by Formula II include o-, m- and p-vinylphenyl boroxoles, and the term "a vinylphenyl boroxole" as used generically herein and in the appended claims includes both the pure or substantially pure isomers of vinylphenyl boroxole, as well as any two or all three of the aforementioned isomers in any proportions.

The vinylphenyl boronates of this invention are the salts or esters of a vinylphenyl boronic acid of the kind embraced by Formula I. The salts of the invention include, but are not limited to, those which may be represented by the following general formulas

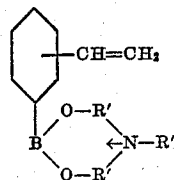
(III)



wherein M represents an alkali metal (e.g., sodium, potassium, lithium, etc.) or the monovalent residue of a strong, organic base, for instance, pentamethylguanidine, the strongly basic quaternary ammonium hydroxides including the various tetralkylammonium hydroxides (e.g., tetramethyl-, tetraethyl-, tetrapropylammonium hydroxides, etc.), the various tetraalkanolammonium hydroxides (e.g., tetraethanolammonium hydroxide, tetrapropanolammonium hydroxide, tetrabutanolammonium hydroxide, etc.), the various benzyltrialkylammonium hydroxides (e.g., benzyltrimethylammonium hydroxide, benzyltriethylammonium hydroxide, etc.), and others that either will be apparent to those skilled in the art from the foregoing illustrative examples or can be ascertained by routine experimentation.

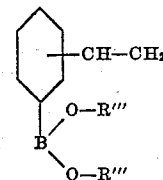
Esters of the vinylphenyl boronic acids within the scope of this invention include, but are not limited to, esters represented by the following general formula

(IV)



wherein R' represents an alkylene radical containing from 2 to 7 carbon atoms, inclusive, and R'' represents a member of the class consisting of hydrogen and hydrocarbon radicals containing from 1 to 7 carbon atoms, inclusive; and esters represented by the following general formula:

(V)



wherein R''' represents a member of the class consisting of hydrocarbon and halogenated hydrocarbon radicals. The term "a vinylphenyl boronate," as used generically herein and in the appended claims includes the salts and esters of both the pure or substantially pure isomers of a vinylphenyl boronic acid, as well as of any two or all three of the isomers (o-, m- and p-isomers) in any proportions; and it is to be understood that this same definition applies to the more specific salts embraced by

Formula III and to the more specific esters embraced by Formulas IV and V.

Illustrative examples of radicals represented by R' in Formula IV, that is, of alkylene (including cycloalkylene) radicals containing from 2 to 7 carbon atoms, inclusive, are: ethylene, propylene (trimethylene), butylene, isobutylene, the various pentylenes (including the normal and isomeric pentylenes), hexylenes (both normal and isomeric forms) and heptylenes including both the normal heptylene and the various isomeric heptylenes; also, cyclopentylene, cyclohexylene and cycloheptylene.

Illustrative examples of hydrocarbon radicals represented by R'' in Formula IV, that is, of hydrocarbon radicals containing from 1 to 7 carbon atoms, inclusive, are: aryl (including cycloalkyl), alkenyl (including cycloalkenyl), aralkyl, aryl, alkaryl and alkenylaryl radicals containing from 1 through 7 carbon atoms. More specific examples of such radicals are methyl, ethyl, propyl to heptyl, inclusive (both normal and isomeric forms), cyclopentyl, cyclopentenyl, cyclohexyl, cyclohexenyl, cycloheptyl, benzyl, phenyl, tolyl, vinyl, allyl, methallyl, propenyl, isopropenyl (beta-allyl), 1-butenyl, 2-butenyl (crotyl), 3-butenyl, pentenyl, hexenyl, heptenyl, butadienyl, etc.

Illustrative examples of hydrocarbon and halogenated hydrocarbon (halohydrocarbon) radicals represented by R''' in Formula V are the same hydrocarbon radicals mentioned above with respect to the definition of R'' in Formula IV and the partly halogenated and perhalogenated forms thereof, that is, partly or completely chlorinated, brominated, iodinated or fluorinated forms thereof and where the halogen is the same or different in the individual radical; and also those hydrocarbon and halohydrocarbon radicals that contain more than 7 carbon atoms such as, for example: octyl to octadecyl, inclusive (both normal and isomeric forms), phenylethyl, phenylpropyl, phenylisopropyl, phenylallyl, biphenyl or xenyl, naphthyl, xylyl, ethylphenyl, propylphenyl, isopropylphenyl, butylphenyl, vinylphenyl, allylphenyl, phenylallyl, phenylmethallyl and other higher alkenylaryl radicals, octenyl to octadecenyl, inclusive, octadienyl, and the corresponding halo-(chloro-, bromo-, iodo- and fluoro-)hydrocarbon radicals, including the partly halogenated and perhalogenated forms thereof, and wherein the halogen is the same or different in the individual radical. The halogen may be in an aliphatic grouping or in an aromatic grouping or in both such groupings when the radical contains both aromatic and aliphatic groupings.

More specific examples of the vinylphenyl boronic esters of this invention are iminodiethyl ester of a vinylphenyl boronic acid, e.g., iminodiethyl(p-vinylphenyl) boronate, N-methyliminodiethyl(p-vinylphenyl) boronate, the various dialkyl and dialkenyl esters of a vinylphenyl boronic acid, for instance the dibutyl and diallyl esters thereof, and specifically di-n-butyl(p-vinylphenyl) boronate and diallyl(p-vinylphenyl) boronate, and others that will be apparent to those skilled in the art from the foregoing illustrative examples and from the illustrative examples hereinbefore given of radicals represented by R' and R'' in Formula IV and of radicals represented by R''' in Formula V.

The vinylphenyl boronic acids, the vinylphenyl boroxoles and the vinylphenyl boronates of this invention are useful as chemical intermediates and in numerous other applications where compounds containing boron in the molecule are useful. They may be employed as the active ingredient in, or as a useful additive to, a large variety of compositions including insecticides, bactericides, germicides, fungicides, pesticides and the like. They are particularly useful when homopolymerized and copolymerized. They can be copolymerized with each other and with other copolymerizable ingredients, more particularly compounds containing a $\text{CH}_2=\text{C}<$ grouping, as

disclosed and claimed in other copending applications filed concurrently herewith, viz., Serial No. 682,316 of Thomas and Hoffmann directed to the production of homopolymers and copolymers of a vinylphenyl boronic acid; 5 Serial No. 682,315 of Hoffmann and Thomas directed to the production of homopolymers and copolymers of a vinylphenyl boroxole; and Serial No. 682,326 of Hoffmann and Thomas directed to the production of homopolymers and copolymers of a vinylphenyl boronate.

10 Various methods can be used in producing the vinylphenyl boronic acids, the vinylphenyl boroxoles and the vinylphenyl boronates of this invention. One general procedure for the preparation of each is described briefly below:

15 The o-, m- and p-vinylphenyl boronic acids (or mixtures of any two or all three of these isomers in any proportions) can be prepared by hydrating the corresponding vinylphenyl boroxole.

20 The o-, m- and p-vinylphenyl boroxoles (or mixtures of any two or all three of these isomers in any proportions) can be prepared by dehydrohalogenating, under anhydrous conditions and while admixed with a base, the corresponding alpha-X-ethylphenyl boroxole where X represents chlorine or bromine.

25 The o-, m- and p-vinylphenyl boronates (i.e., o-, m- and p-vinylphenyl boronic salts and the o-, m- and p-vinylphenyl boronic esters), and mixtures of any two or all three of the aforesaid isomers in any proportions, can be prepared by techniques which, in general, are essentially the same as those commonly employed in preparing salts and esters of other polymerizable, organic or organo-metallic, monomeric acids and anhydrides.

30 Thus, salts of a vinylphenyl boronic acid can be made by contacting the corresponding boronic acid (or the corresponding boroxole) with a base capable of forming a salt therewith. Numerous examples of such bases have been given hereinbefore in connection with the definition of M in Formula III. More particularly, one can prepare salts of the kind embraced by Formula III by adding to 1 mole of a vinylphenyl boronic acid, or to 1/3 35 mole of a vinylphenyl boroxole, an appropriate quantity, e.g., about 500 ml., of an aqueous solution of an alkali-metal hydroxide (sodium, potassium, lithium, etc., hydroxide) containing, for instance, from 2 to 5 moles of the base. The boronic acid dissolves, as does also the boroxole if the latter has been used. Or, instead of the alkali-metal hydroxide solution, one can substitute an appropriate quantity, e.g., about 1 liter, of an aqueous solution containing about 1 mole of a strong, organic 40 base, for instance a strongly basic quaternary ammonium hydroxide such as, for example, tetraethanolammonium hydroxide (or any of the other quaternary ammonium hydroxides mentioned hereinbefore by way of example). Acidification with hydrochloric acid or any other water-soluble mineral acid reprecipitates the vinylphenyl boronic acid.

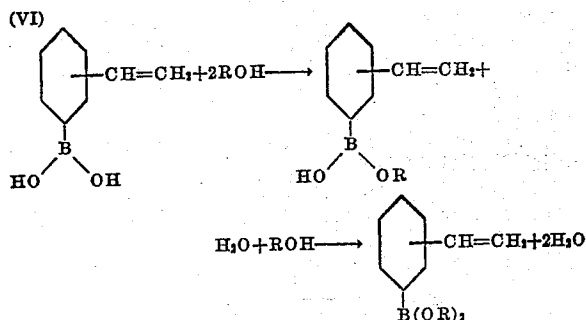
45 Esters of a vinylphenyl boronic acid can be prepared by, for example, reacting an alcohol at the boiling temperature of the reaction mass with a vinylphenyl boronic acid or a vinylphenyl boroxole (anhydride of a vinylphenyl boronic acid) until the desired degree of esterification has been effected, more particularly until water no longer is evolved. After removing any unreacted 50 alcohol, the formed ester, e.g., the monohydric alcohol diester or the polyhydric (e.g., di-, tri-, tetra- and pentahydric, etc.) alcohol ester of a vinylphenyl boronic acid, or whatever the ester may be that is being prepared, can be isolated from the reaction mass, if desired, by any suitable means. For example, the esters which are distillable without decomposition can be isolated by distillation under reduced pressure, using fractional distillation to purify them.

55 In the case of the polyhydric alcohol esters of a vinylphenyl boronic acid or the anhydride thereof, the poly-

hydric alcohol ester advantageously, in some cases, may be allowed to remain in the reaction mass and used as such, with or without the removal of any excess alcohol, e.g., by distillation, solvent extraction or esterification in situ with a different organic or organo-metallic acid, for instance, phthalic acid or anhydride, maleic acid or anhydride, fumaric acid, succinic acid, adipic acid or other saturated or unsaturated polycarboxylic acid or anhydride; or with a monocarboxylic acid, e.g., acetic, propionic, valeric, oleic, palmitic, stearic, etc.

Esters also may be made by ester exchange reactions in the presence of a suitable catalyst, using an ester of a lower boiling alcohol, such as a dimethyl or a diethyl ester of a vinylphenyl boronic acid, and an alcohol corresponding to the ester desired.

In the preparation of the esters of this invention it is believed that the reaction proceeds stepwise in accordance with the following general equations, and for purpose of simplicity the reaction is shown as taking place between a vinylphenyl boronic acid and a monohydric alcohol:



The monoester, however, is difficult to isolate, probably because of its disproportionation into the corresponding boronic acid and diester. A given amount of monoester may exist, however, in solution if to one mole of a boronic acid be added 1 mole of a monohydric alcohol.

Similar to monoesters, mixtures of symmetrical diesters and unsymmetrical diesters may coexist in solution. The proportions in which they are present (under any given set of conditions) are governed by their relative thermodynamic stabilities. If, for example, 1 mole each of n-butanol and n-octanol be added to 1 mole of a vinyl phenyl boronic acid, it is probable that a mixture of di-n-butyl(vinylphenyl)boronate, di-n-octyl(vinylphenyl)boronate and n-butyl-n-octyl(vinylphenyl)boronate would be present in solution. Fractional distillation of the esters, however, would probably lead (with disproportionation of the unsymmetrical ester) to removal of the lower boiling symmetrical diester, followed by the higher boiling symmetrical diester. In the event that two alcohols give symmetrical diesters having the same (or very nearly the same) boiling point, it is probable that the unsymmetrical diester, if having a boiling point near that or lower than that of the symmetrical esters, could be obtained by distillation.

In making the esters by direct esterification, or by other alternative techniques, the reaction is preferably effected while the reactants are contained in an inert, organic, liquid medium, e.g., benzene, toluene, etc., thereby to aid in the removal of water in instances where water is evolved as a by-product. In some cases an excess of the alcohol reactant may constitute the organic liquid medium in which the reaction is effected. An inhibitor of polymerization, e.g., ascorbic acid, hydroquinone, copper in the form of filings or turnings, or other known inhibitors of vinyl-type polymerization reactions, advantageously may be added to the reaction mass either initially, or during a later stage of the process, in order to inhibit or minimize the formation of a homopolymer of the ester of the vinylphenyl boronic acid. An esterification catalyst, e.g., potassium or other alkali-metal carbonate, may

sometimes be used advantageously in order to initiate the reaction more quickly.

We prefer to prepare the esters of this invention by direct esterification of a vinylphenyl boronic acid or the corresponding boroxole with an alcohol corresponding to the ester desired, usually at a temperature not exceeding substantially about 200° C. In the preparation of the esters an excess of the alcohol over that theoretically required for reaction with the vinyl phenyl boronic acid or anhydride to form the ester ordinarily is employed, but equivalent molar proportions may be used, if desired; that is, two moles of the monohydric alcohol per mole of the vinylphenyl boronic acid or six moles of the monohydric alcohol per mole of the vinylphenyl boroxole. The resulting esterification product can be purified by suitable means, e.g., by distillation.

Examples of monohydric alcohols that can be used in making the vinylphenyl boronic esters of this invention are the methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl alcohols, and the higher members of the homologous series up to and including octadecyl alcohol in the normal and various isomeric forms, and even higher, e.g., those containing as many as, say, 30 carbon atoms in the molecule; benzyl, phenylethyl and other aralkyl alcohols; the various monohydric cycloaliphatic alcohols, e.g., cyclohexanol, methylcyclohexanol, etc.; the various available (or relatively simple to make) unsaturated monohydric alcohols, e.g., allyl, methallyl, ethallyl, crotyl and cinnamyl alcohols, 3-hydroxybutene-1, etc., and halogenated (chlorinated, brominated, fluorinated or iodinated) alcohols corresponding to those just mentioned by way of example, e.g., 1-chloroallyl alcohol, 2-chloroallyl alcohol, 1-bromoallyl alcohol, 2-bromoallyl alcohol, 1,2-dichloroallyl alcohol, 1,2-dibromoallyl alcohol, 1,2-difluoroallyl alcohol, 2-chloropropanol-1, 3-chloropropanol-1, 3-iodopropanol-1, 2,3-dichloropropanol-1, etc.; the various nuclearily halogenated (chlorinated, brominated, etc.) benzyl alcohols; the various available monohydric nitroalcohols; the various monohydric silanols; and others that will be apparent to those skilled in the art from the foregoing illustrative examples.

Examples of polyhydric alcohols that can be used either alone or in conjunction with a monohydric alcohol in preparing the esters of this invention are ethylene glycol, di-, tri- and tetraethylene glycols, propylene glycol, tetramethylene glycol, hexamethylene glycol, octamethylene glycol, decamethylene glycol, dodecamethylene glycol, glycerol, thiodiglycol, pentaerythritol, dipentaerythritol, neopentyl glycol, dineopentyl glycol, trimethylol propane, 1,4-butanediol, 2-butene-1,4-diol, 2-butyne-1,4-diol, 2-ethyl-1,3-hexanediol, pentaethylene glycol, hexaethylene glycol, octaethylene glycol, decaethylene glycol, 2-butyl-1,3-octanediol, 2-ethyl-2-methylol-1-hexanol (2-ethyl-2-butyl-1,3-propanediol), 6-methyl-2,4-heptanediol, polyallyl and polymethallyl alcohols containing an average of at least five primary hydroxyl groups per molecule, dipropylene glycol, dibutylene glycol, dihexylene glycol, di-(2-hydroxyamyl)ether; and halogenated (chlorinated, brominated, fluorinated or iodinated) polyhydric alcohols corresponding to those just mentioned by way of example, e.g., 2-chloro-1,3-hexanediol, 2-bromo-1,3-octanediol, 2,2-dichloro-1,3-propanediol, 2,2-dibromo-1,3-propanediol, 2-fluoro-1,3-hexanediol, 2-iodo-2-butyl-1,3-propanediol, perfluorinated polymeric allyl alcohol containing an average of at least five primary hydroxyl groups per molecule; and others that will be apparent to those skilled in the art from the foregoing illustrative examples.

To the best of our knowledge and belief any monohydric alcohol and any polyhydric alcohol are operative in producing the esters of this invention.

Advantageously the alcohol employed is one in which the hydroxyl group or groups are the only substituents thereof which are reactive in an esterification reaction.

In order that those skilled in the art may better under-

stand how the present invention can be carried into effect, the following examples are given by way of illustration and not by way of limitation. All parts and percentages are by weight unless otherwise stated.

EXAMPLE 1

Preparation of *p*-vinylphenyl boronic acid

This example illustrates the preparation of *p*-vinylphenyl boronic acid by dehydrobromination of *p*- α -bromoethylphenyl boroxole.

A. PREPARATION OF INTERMEDIATES USED IN MAKING *p*- α -BROMOETHYLPHENYL BOROXOLE

(a) *p*-Ethylbromobenzene.—To two kg. (18.85 moles) of ethylbenzene contained in a 5-liter, 3-necked, round-bottom flask equipped with a stirrer, addition funnel, reflux condenser and hydrogen-bromide trap, are added 100 g. of iodine and 3 g. of steel wool. Following solution of the iodine, 3,083 g. (19.25 moles) of bromine are added at a rate such that the temperature of the reaction mixture does not exceed 60° C. After hydrogen-bromide evolution has ceased following completion of the bromine addition, the reaction mass is washed with excess 10% aqueous sodium hydroxide solution, and then with 10% aqueous sodium thiosulfate solution until colorless. After drying over solid sodium hydroxide, the product is distilled to obtain 3,306 g. (92% of the theoretical yield), B.P., 196°–215° C. The mixture of isometric bromides is then fractionally distilled to separate the *o*- and *p*-isomers; pure para isomer, n_D^{25} 1.5425.

(b) *p*-Ethylphenylboronic acid.—*p*-Ethylbromobenzene, 555 g. (3.0 moles), is added dropwise to 73 g. (3.15 moles) Mg in 1 liter of anhydrous ether (diethyl ether). After completion of the reaction, the ether solution of *p*-ethylphenylmagnesium bromide is added dropwise under nitrogen pressure to a solution of 913 g. (3.98 moles) of *n*-butyl borate (tri-*n*-butyl borate) in 800 ml. of anhydrous ether cooled to -70° C. in a Dry Ice-acetone bath. After the addition of the Grignard solution has been completed, the reaction mixture is allowed to warm slowly to room temperature. The reaction mass is allowed to remain at ambient temperature for 12 hours before decomposition.

The reaction mass is decomposed by the addition of 1 liter of 10% aqueous sulfuric acid. The ether layer is separated, and evaporated on a water bath. Following the removal of ether, the butanol-water system is made alkaline with aqueous sodium hydroxide solution, and the butanol is removed by distillation in vacuo. Water is added from time to time to maintain a volume of about 3 liters. When the butanol has been removed, the aqueous solution is acidified with hydrochloric acid, and the resultant precipitate of *p*-ethylphenylboronic acid is filtered off, and recrystallized once from hot water. Yield: 378 g. 84% of the theoretical yield; M.P. 149°–150° C.

(c) *p*-Ethylphenylboroxole.—*p*-Ethylphenylboronic acid, 284 g. (1.9 moles), is refluxed in 1 liter of toluene in a flask fitted with a Dean and Stark trap to remove water. When water no longer appears in the condensate, the toluene is removed by vacuum evaporation to yield crystalline *p*-ethylphenylboroxole, M.P. 194°–195° C.

b. PREPARATION OF *p*- α -BROMOETHYLPHENYL BOROXOLE

p-Ethylphenylboroxole, 147 g. (0.372 mole), is dissolved in 3.25 liters of anhydrous carbon tetrachloride. *N*-bromosuccinimide, 200 g. (1.125 moles), is added and the reaction mixture is heated to reflux. A free-radical catalyst, specifically benzoyl peroxide, 1.0 g., is then added to initiate the reaction. In the absence of such a catalyst more than 8 hours is required before reaction begins, while in the presence of an initiating or catalytic amount of benzoyl peroxide bromination is complete in about 3 hours. After completion of the reaction the by-

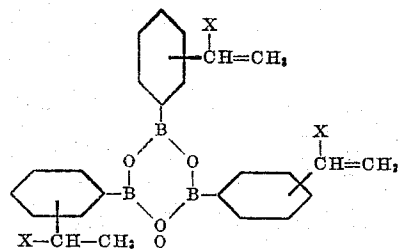
product succinimide, which is insoluble in carbon tetrachloride, is removed by filtration, washed with small portions of carbon tetrachloride and the solvent removed from the filtrate by evaporating it on a water bath.

5 Cooling the residue results in the formation of a pale tan, crystalline mass of crude *p*- α -bromoethylphenyl boroxole which, on recrystallization from 1:1 benzene-cyclohexane (by volume), yields 212 g. (90% of theory) of cream-colored product. An additional recrystallization provides a white product, M.P. 183.5°–184° C.

10 *Analysis*.—Calc'd for $C_{24}H_{24}O_3Br_3B_3$: C, 45.56; H, 3.82; Br, 37.90; B, 5.13. Found: C, 45.51; H, 3.97; Br, 38.16; B, 5.09.

The *p*- α -chloroethylphenyl boroxole is prepared by following the same procedure described above with reference to the preparation of *p*- α -bromoethylphenyl boroxole with the exception that, instead of using 1.125 moles of *N*-bromosuccinimide, there are employed 1.125 moles of *N*-chlorosuccinimide. The crude product, *p*- α -chloroethylphenyl boroxole, is purified likewise as described above with reference to the corresponding bromoethylphenyl boroxole. A good yield of purified product is obtained. This compound can be used in the same manner described below with reference to the preparation of *p*-vinylphenyl boronic acid from *p*- α -bromoethylphenyl boroxole.

In the copending application of Arthur K. Hoffmann, Serial No. 682,313, filed concurrently herewith, now Patent No. 2,868,840, dated January 13, 1959, claims are made to compounds represented by the general formula



where X represents a halogen selected from the class consisting of chlorine and bromine, and to a method of preparing the same.

c. PREPARATION OF *p*-VINYLPHENYL BOROXOLE AND *p*-VINYLPHENYL BORONIC ACID

p- α -Bromoethylphenyl boroxole, 10 g. (0.0155 mole), is placed in a 150 ml. Erlenmeyer flask to which 20 g. of a base, specifically freshly distilled quinoline is added. The reaction mixture is heated at 130°–140° C. for one-half hour with occasional stirring. During the reaction the flask is protected by a calcium sulfate drying tube. At the end of the reaction time, the flask is cooled and the contents comprising *p*-vinylphenyl boroxole is poured into 200 ml. of water to hydrate the boroxole. The reaction mass is acidified with aqueous hydrochloric acid and extracted with ether (diethyl ether). The ether is evaporated on the water bath and the residual, light-orange solid recrystallized from hot water in the presence of a small amount of charcoal. The yield of colorless *p*-vinylphenyl boronic acid (hydrated *p*-vinylphenyl boroxole) is 5.3 g. (74% of theory); M.P., 179°–182° C., dec.

Instead of quinoline one can use any other base as a hydrohalide acceptor, for instance bases such as were mentioned above in connection with the definition of M in Formula III. Additional examples are calcium hydroxide, barium hydroxide, ammonium hydroxide, etc.; carbonates of inorganic bases, including the carbonates of alkali metals; other organic amines in addition to pyridine, e.g., trimethyl amine, triethyl amine, tributyl amine, dimethyl aniline, etc.; and the like.

The *o*- and *m*-vinylphenyl boronic acids are prepared from the corresponding *o*- and *m*- α -bromoethylphenyl boroxoles in essentially the same manner described above

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with reference to the preparation of p-vinylphenyl boronic acid from p-alpha-bromoethylphenyl boroxole.

EXAMPLE 2

Preparation of o-vinylphenyl boroxole and o-vinylphenyl boronic acid

O-Alpha-bromoethylphenyl boroxole is prepared from the corresponding ortho derivative in exactly the same manner as described above with reference to the preparation of the para isomer; and o-vinylphenyl boroxole and o-vinylphenyl boronic acid are produced therefrom by following the identical procedure described under Example 1-C for the preparation of the para derivatives. The product is soluble in aqueous sodium hydroxide and absorbs bromine, showing unsaturation to be present in the molecule.

The m-vinylphenyl boroxole and m-vinylphenyl boronic acid can be similarly prepared from the corresponding meta derivatives.

Examples 3 to 8, inclusive, which follow, illustrate a different method of preparing the vinylphenyl boroxoles, namely, by dehydrating the corresponding vinylphenyl boronic acid until water is no longer evolved; and is more fully disclosed, and broadly and specifically claimed, in the copending application of Stephen J. Groszos and Arthur K. Hoffmann, Serial No. 682,314, filed concurrently herewith.

EXAMPLE 3

p-Vinylphenyl boronic acid, 10 g. (0.068 mole), is refluxed in 200 ml. of toluene till water is no longer evolved, using a flask fitted with a Dean and Stark trap to remove the water. Evaporation of the toluene to a volume of 20 ml., leads to the deposition of 8.4 g. of pale tan crystals of p-vinylphenyl boroxole. Yield, 97% of theory. Two recrystallizations of a small sample of the product from toluene afford colorless needles, M.P. 195°-196° C.

Analysis.—Calc'd. for $C_{24}H_{21}B_3O_3$: C, 73.93; H, 5.43; B, 8.33. Found: C, 73.94; H, 5.45; B, 8.54.

EXAMPLE 4

Example 3 is repeated using 200 ml. of benzene instead of 200 ml. of toluene, and continuing to reflux the dispersion of the p-vinylphenyl boronic acid in the benzene until water no longer is evolved. The yield of crude crystals of p-vinylphenyl boroxole is more than 95% of the theoretical.

EXAMPLE 5

The same procedure is followed as described under Example 3 with the exception that 10 g. of o-vinylphenyl boronic acid is used instead of 10 g. of the para isomer. The yield of crystalline o-vinylphenyl boroxole is approximately 97% of the theoretical.

EXAMPLE 6

p-Vinylphenyl boronic acid, 10 g. (0.068 mole), is heated in vacuo to 150° C. in an oil bath for 3 hours. At the end of this time, the evacuated vessel is cooled and dry air admitted. The yield of crude, pale yellow p-vinylphenyl boroxole is quantitative, and two recrystallizations from toluene afford colorless, crystalline product.

EXAMPLE 7

Example 5 is repeated using 250 ml. of o-xylene instead of 200 ml. of toluene. The dispersion of o-vinylphenyl boronic acid in o-xylene is refluxed till water no longer appear in the condensate. The o-xylene is then removed by vacuum evaporation. Crude, pale yellow o-vinylphenyl boroxole is obtained in a yield of approximately 95% of theory.

EXAMPLE 8

Example 3 is repeated using 300 ml. of propionitrile instead of 200 ml. of toluene. The solution of p-vinyl-

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phenyl boronic acid is slowly distilled till the volume of distillate is 50 ml. The remainder of the solvent is removed by vacuum evaporation. The yield of crude p-vinylphenyl boroxole is about 98% of theory.

Examples 9, 10, 11, 12 and 13, which follow, illustrate the preparation of typical vinylphenyl boronic salts of the invention.

EXAMPLE 9

To one mole of p-vinylphenyl boronic acid is added about 500 ml. of a 2-molar solution of sodium hydroxide in water. The vinylphenyl boronic acid dissolves, and the sodium salt thereof is formed. Acidification with hydrochloric acid or with any other water-soluble mineral acid reprecipitates the p-vinylphenyl boronic acid.

EXAMPLE 10

Same as in Example 9 with the exception that there is used 1/3 mole of p-vinylphenyl boroxole instead of 1 mole of p-vinylphenyl boronic acid, and 500 ml. of a 5-molar (instead of 2-molar) solution of sodium hydroxide in water. Similar results are obtained.

EXAMPLE 11

Same as in Example 9 with the exception that there is used one mole of o-vinylphenyl boronic acid instead of the para isomer, and about 500 ml. of a 3-molar solution of potassium hydroxide in water in place of a 2-molar solution of sodium hydroxide in water. Similar results are obtained.

EXAMPLE 12

Example 9 is repeated but using, as the base, 1 liter of an aqueous solution containing 1 mole of tetraethanolammonium hydroxide instead of a 2-molar solution of sodium hydroxide in water. Similar results are obtained.

EXAMPLE 13

Same as in Example 9 with the exception that 1/3 mole of o-vinylphenyl boroxole is used in place of 1 mole of p-vinylphenyl boronic acid, and 1 liter of an aqueous solution of the base as in Example 12 instead of a 2-molar solution of sodium hydroxide in water. Similar results are obtained.

The remaining examples illustrate the preparation of various esters of the invention.

EXAMPLE 14

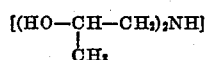
p-Vinylphenyl boronic acid, 5.0 g. (0.034 mole), is subjected to azeotropic distillation in 200 ml. of toluene containing 3.6 g. (0.034 mole) diethanolamine for 2 hours. At the end of this time, the reaction mass is cooled and filtered. Recrystallization of the colorless product from acetone yields 7.3 g. (99% of theory) of long, glistening needles of iminodiethyl(p-vinylphenyl) boronate. M.P. 236°-137° C., dec.

Analysis.—Calc'd. for $C_{12}H_{16}O_2NB$: C, 66.39; H, 7.43; N, 6.45; B, 4.98. Found: C, 66.42; H, 7.41; N, 6.44; B, 5.06.

If desired, a polymerization inhibitor can be included with the primary reactants, e.g., from about 0.005 g. to 0.05 g. of hydroquinone, pyrogallol, ascorbic acid, iso-ascorbic acid and/or other inhibitor of vinyl-type polymerizations.

EXAMPLE 15

Iminodiisopropyl(o-vinylphenyl) boronate is prepared by following exactly the same procedure employed in Example 1 with the exception that, instead of the reactants used in that example, there are used 0.034 mole of o-vinylphenyl boronic acid and 0.034 mole of diisopropanolamine



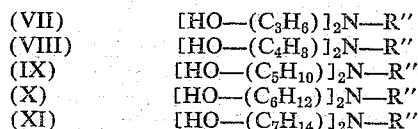
The yield of iminodiisopropyl(o-vinylphenyl) boronate is above 95% of the theoretical.

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EXAMPLE 16

p-Vinylphenyl boronic acid, 10.0 g. (0.068 mole), is subjected to azeotropic distillation in toluene with 8.5 g. (0.071 mole) of N-methyldiethanolamine. The toluene, after water has ceased to distill, is removed by evaporation in vacuo and the crude ester recrystallized from cyclohexane. A high yield of N-methyliminodiethyl(o-vinylphenyl) boronate is obtained. Its identity is established by infrared examination.

Instead of N-methyldiethanolamine in the above formulation one can use any other N-(hydrocarbon)diethanolamine wherein the hydrocarbon substituent contains from 2 to 7 carbon atoms, inclusive, or any of the amines represented by the following general formulas:



In Formulas VII through XI R'' represents a hydrocarbon radical containing from 1 to 7 carbon atoms, inclusive, numerous examples of which have been given hereinbefore.

o-Vinylphenyl boronic acid and/or m-vinylphenyl boronic acid can be used in lieu of or in combination with p-vinylphenyl boronic acid in the above example, and any one or two or all of them can be employed as a reactant with any of the above-defined N-(hydrocarbon)dialkanolamines.

EXAMPLE 17

p-Vinylphenyl boronic acid (8.25 g.) and 11.9 g. of benzyl alcohol in toluene are subjected to azeotropic distillation for 2 hours. The toluene is distilled off and the pure ester, dibenzyl(p-vinylphenyl) boronate, is obtained as a viscous liquid by molecular distillation at 1 mm. pressure. The product is stabilized with hydroquinone to prevent homopolymerization. Hydroquinone or other polymerization inhibitor in a suitable amount (e.g., in an amount corresponding to from 0.1% to 1% by weight of the vinylphenyl boronic acid) may be incorporated into the reaction mixture prior to or during the esterification reaction, or prior to or during isolation of the formed ester.

EXAMPLE 18

About 15 g. of p-vinylphenyl boronic acid is azeotroped (that is, subjected to azeotropic distillation) in 200 ml. of toluene for 1 hour to form the corresponding boroxole. To the toluene solution is added 225 ml. of freshly distilled allyl alcohol and the solution is azeotroped. When water no longer appears in the distillate, the toluene and excess allyl alcohol are removed by distillation at atmospheric pressure, and the residue is distilled in vacuo to obtain diallyl(p-vinylphenyl) boronate as a fraction boiling at 100° C. at 1 mm. pressure.

Instead of p-vinylphenyl boronic acid one can use o- and/or m-vinylphenyl boronic acid, or a mixture of either or both with p-vinylphenyl boronic acid. With these boronic acids as such or in the form of the corresponding boroxoles, and also with p-vinylphenyl boronic acid or boroxole, one can directly esterify with methyl alcohol (instead of all or part of the allyl alcohol in the above example) or with any other unsaturated monohydric alcohol, or with furfuryl alcohol, or with any of the other alcohols hereinbefore mentioned by way of example.

EXAMPLE 19

Example 19 is repeated exactly, but additionally there is included in the reaction mixture 1 g. of hydroquinone as a polymerization inhibitor. A slightly higher yield of monomeric diallyl(p-vinylphenyl) boronate is obtained.

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EXAMPLE 20

p-Vinylphenyl boronic acid, 15.0 g. (0.10 mole), is azeotroped in 100 ml. of n-butanol for about 3½ hours. The butanol is removed by distillation at atmospheric pressure, followed by vacuum evaporation at 100° C. The residue is distilled under reduced pressure to obtain di-n-butyl(p-vinylphenyl) boronate as a fraction boiling at 130° C. at 1 mm. pressure. The yield of ester is 14.4 g., which corresponds to about 55% of the theoretical.

EXAMPLE 21

p-Vinylphenyl boronic acid (29.8 g.; 0.201 mole) and 39.3 g. (0.416 mole) of 3-chloropropanol-1 in toluene are subjected to azeotropic distillation. The toluene is removed by distillation at atmospheric pressure and di-(3-chloropropyl)(p-vinylphenyl) boronate is collected as the fraction boiling at 138° C. at 1 mm. pressure. The isolated ester must be inhibited with hydroquinone or other polymerization inhibitor; otherwise, it rapidly polymerizes.

Somewhat higher yields of monomeric di-(3-chloropropyl)(p-vinylphenyl) boronate are generally obtained when an inhibiting amount of a polymerization inhibitor is incorporated into the reaction mass prior to or during esterification, or prior to or during isolation of the formed ester; for example, by adding 0.3 to 0.7 g. of pyrogallol.

EXAMPLE 22

A round-bottomed flask is fitted with a heating mantle, a condenser and a Dean and Stark trap to remove water of reaction. The flask is charged with 18.8 parts of dry phenol, 14.8 parts of p-vinylphenyl boronic acid and 100 parts of dry toluene. The mixture is heated for 12 hours under reflux, water of reaction being retained in the trap. At this point the odor of phenol has disappeared and infrared analysis indicates the presence of B—O—C linkages. Due to ease of hydrolysis or (on long heating) to partial conversion to the corresponding boroxole, the crude product, which comprises a mixture of mono-phenyl(p-vinylphenyl)boronate and diphenyl(p-vinylphenyl) boronate, is not isolated but is used directly in toluene solution.

Instead of all, or in lieu of part of, the p-vinylphenyl boronic acid in the above example, one can use the o-isomer and/or the p-isomer.

EXAMPLE 23

Dicyclohex-2-enyl(p-vinylphenyl)boronate is prepared by the following procedure:

To a flask equipped with a Dean and Stark trap are charged 74 parts of p-vinylphenyl boronic acid and 49 parts of cyclohex-2-ene-1-ol. To the mixture is added 200 parts of n-nonane, and the dispersion is heated with refluxing for 4 hours. It is desirable to conduct the esterification process and subsequent isolation of product in the presence of 1 to 2 parts of hydroquinone as a polymerization inhibitor. In the absence of inhibitor, the yield of final ester is significantly lower. At the end of the reflux time, the reaction mass is homogeneous and the flask is connected to a downward condenser. n-Nonane, 100 parts, is collected at atmospheric pressure. The remainder of the nonane is removed by vacuum evaporation at 1 mm. pressure. The cooled viscous residue comprising dicyclohex-2-enyl(p-vinylphenyl)boronate is purified by short path distillation at 1 mm., after 0.2 g. of t-butyl catechol has been added to it.

Instead of the particular monohydric alcohols (monohydroxy compounds) employed in the above illustrative examples of the preparation of the esters of this invention, one can use any other such alcohol of which numerous examples have been given hereinbefore. Additional examples of monohydroxy compounds that can be employed in making esters of the present invention, for instance by methods such as are illustrated by the fore-

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going examples directed to ester formation, are the following:

Ethylene glycol monomethyl ether
 Ethylene glycol monoethyl ether
 Ethylene glycol monopropyl ether
 Ethylene glycol monobutyl ether
 Ethylene glycol monophenyl ether
 Ethylene glycol monoethyl thioether
 Diethylene glycol monomethyl ether
 Diethylene glycol monoethyl ether
 Diethylene glycol monobutyl ether
 Ethylene chlorohydrin
 Ethylene bromohydrin
 Ethylene cyanohydrin
 Ethylene glycol monoacetate
 Ethylene glycol monopropionate
 Ethylene glycol monobenzoate
 Diethylene glycol monoacetate
 Ethylene glycol monoallyl ether
 Ethylene glycol monomethyl ether
 Beta-nitroethanol
 Beta-dimethylaminoethanol
 Hydroxy acetone
 Methyl beta-hydroxyethyl ketone
 Ethyl hydracrylic ester
 2-methoxy-1-propanol
 2-ethoxy-1-propanol
 2-butoxy-1-propanol
 2-bromo-1-propanol
 1-bromo-2-propanol
 Trimethylene glycol monomethyl ether
 Gamma-chloro-1-propanol
 2-nitro-2-methyl-1-propanol

Likewise, in place of the particular vinylphenyl boronic acid employed in the individual example, one can use any other isomer or mixtures thereof in any proportions.

EXAMPLE 24

A glyceryl p-vinylphenyl boronate is prepared as follows:

To a reaction vessel provided with means for the continuous withdrawal of water of condensation are charged 581 parts of glycerol, 374 parts of p-vinylphenyl boroxole and 2 parts of hydroquinone as a polymerization inhibitor. The vessel is flushed with nitrogen gas prior to charging the reaction vessel, and the reaction is carried out in an atmosphere of nitrogen.

The reaction mixture is heated with the discharge of condensation water to 215° C. It is then further heated at 215°-225° C. until no more water is evolved and for about ½ to 1 hour thereafter. The resulting glyceryl ester is a viscous resin.

Instead of 374 parts of p-vinylphenyl boroxole in the above formulation one can use about 428 parts of p-vinylphenyl boronic acid and obtain similar results.

Any or all of the isomers of vinylphenyl boroxole (or boronic acid) can be used in place of the particular isomer used in this example.

EXAMPLE 25

One hundred and twenty-four (124) parts of ethylene glycol and 141 parts of p-vinylphenyl boronic acid are heated together under a nitrogen atmosphere and at a slowly rising temperature for 3 hours to 200° C. under conditions allowing for the discharge of water. It is then held at this temperature for about 2 more hours, or until no more water is being evolved and for about 15 to 45 minutes thereafter. The resulting ester, when cooled to room temperature, is a viscous material.

The vinylphenyl boron compound of this invention have the common characteristic that each has a boron atom which is ortho, meta or para to a vinyl group in a phenyl nucleus. Their reactivities are different from those vinyl monomers wherein the vinyl grouping is attached directly to an aliphatic chain, e.g., an aliphatic hydrocarbon chain.

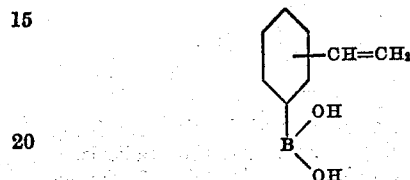
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In our copending application Serial No. 834,643, filed August 19, 1959, as a division of the instant application, claims are made to the method, disclosed herein, of preparing a vinylphenyl boroxole which comprises dehydro-halogenating, under anhydrous conditions and while admixed with a base, the corresponding alpha-X-ethylphenyl boroxole where X represents a halogen selected from the class consisting of chlorine and bromine.

We claim:

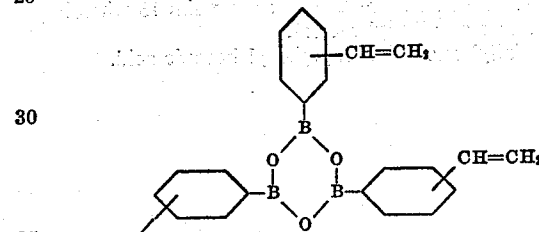
1. A compound of the class consisting of the vinylphenyl boronic acids, the vinylphenyl boroxoles and the vinylphenyl boronates.

2. A vinylphenyl boronic acid represented by the general formula



3. p-Vinylphenyl boronic acid.

4. A vinylphenyl boroxole represented by the general formula

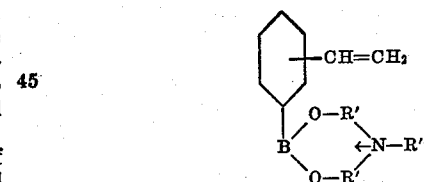


5. p-Vinylphenyl boroxole.

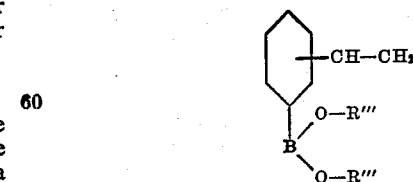
6. A vinylphenyl boronate.

7. A vinylphenyl boronic ester.

8. A vinylphenyl boronic ester selected from the class consisting of (a) vinylphenyl boronic esters represented by the general formula

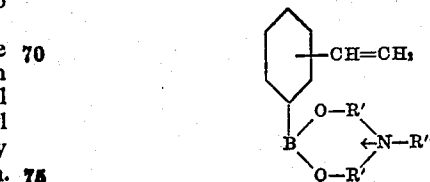


wherein R' represents an alkylene radical containing from 2 to 7 carbon atoms, inclusive, and R'' represents a member of the class consisting of hydrogen and hydrocarbon radicals containing from 1 to 7 carbon atoms, inclusive, and (b) vinylphenyl boronic esters represented by the general formula



wherein R''' represents a member of the class consisting of hydrocarbon and halogenated hydrocarbon radicals.

9. A vinylphenyl boronic ester represented by the general formula



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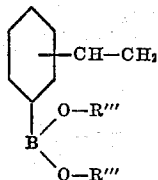
wherein R' represents an alkylene radical containing from 2 to 7 carbon atoms, inclusive, and R'' represents a member of the class consisting of hydrogen and hydrocarbon radicals containing from 1 to 7 carbon atoms, inclusive.

10. A vinylphenyl boronic ester as in claim 9 wherein R'' represents hydrogen.

11. Iminodiethyl ester of a vinylphenyl boronic acid.

12. Iminodiethyl(p-vinylphenyl) boronate.

13. A vinylphenyl boronic ester represented by the general formula



wherein R''' represents a member of the class consisting of hydrocarbon and halogenated hydrocarbon radicals.

14. A vinylphenyl boronic ester as in claim 13 wherein R''' represents an alkyl radical.

15. A dibutyl ester of a vinylphenyl boronic acid.

16. Di-n-butyl(p-vinylphenyl) boronate.

17. A vinylphenyl boronic ester as in claim 13 wherein R''' represents an alkenyl radical.

18. A diallyl ester of a vinylphenyl boronic acid.

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19. Diallyl(p-vinylphenyl) boronate.

20. The method of preparing a vinylphenyl boronic ester which comprises reacting an alcohol at the boiling temperature of the reaction mass with a member of the class consisting of the vinylphenyl boronic acids and the vinylphenyl boroxoles until the desired degree of esterification has been effected; and isolating the resulting vinylphenyl boronic ester from the reaction mass.

21. A method as in claim 20 wherein the reaction is effected while the reactants are contained in an inert, organic liquid medium.

22. A method as in claim 20 wherein the reaction mass contains an inhibitor of polymerization.

References Cited in the file of this patent

UNITED STATES PATENTS

2,248,512	Philip et al.	July 8, 1941
2,443,217	Amos et al.	June 15, 1948

OTHER REFERENCES

Melnikov et al.: Chem. Abs., vol. 33, page 4970 (1939).

Brindley et al.: J. Chem. Society (London), pages 2956-8 (1955).

Lappert: Chem. Reviews, vol. 56, pages 1006, 1009 (1956) also pages 987-989.

UNITED STATES PATENT OFFICE
Certificate of Correction

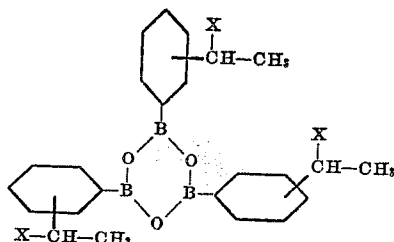
Patent No. 2,934,556

April 26, 1960

Arthur K. Hoffmann et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 57, Formula (V), for that portion reading " $-\text{CH}-\text{CH}_2$ " read " $-\text{CH}=\text{CH}_2$ "; column 3, line 56, for "di-n-butyl(p-vinylphenyl)" read "di-n-butyl(p-vinylphenyl)"; column 5, line 7, for "fumaric" read "fumaric"; same column 5, line 47 and column 6, line 9, for "vinyl phenyl", each occurrence, read "vinylphenyl"; column 7, lines 27 and 28, for "isometric" read "isomeric"; line 55, for "378 g." read "378 g."; line 63, for "b" read "B"; column 8, line 3, for "carbon tetrachloride" read "carbon tetrachloride"; lines 31 to 41, the formula should appear as shown below instead of as in the patent:



same column 8, line 46, for "c" read "C"; column 9, line 17, for "vinylphenyl" read "vinylphenyl"; line 68, for "appear" read "appears"; column 10, line 55, for "137°" read "237°"; column 11, line 55, for "acohol" read "alcohol"; column 13, line 51, for "glyceryl" read "glyceryl"; line 70, for "compound" read "compounds"; column 14, line 58, and column 15, line 14, for " $-\text{CH}-\text{CH}_2$ ", each occurrence, read " $-\text{CH}=\text{CH}_2$ ".

Signed and sealed this 29th day of November 1960.

[SEAL]

Attest:

KARL H. AXLINE,

Attesting Officer.

ROBERT C. WATSON,
Commissioner of Patents.