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CYCLIC ORGANIC COMPOUNDS

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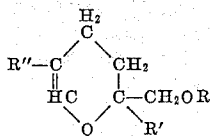
16 Claims. (Cl. 260-333)

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This invention relates to certain novel substituted compounds in the dihydropyran series of compounds, and to a method for their preparation. More particularly, the present invention relates to certain dihydropyran compounds having an oxymethyl group and a hydrocarbyl group directly attached to a single carbon atom of the dihydropyran ring, and to a method for their preparation from alpha-substituted alpha,beta-olefinic aldehydes having a hydrocarbyl group substituted on the alpha carbon atom. Certain derivatives of the novel dihydropyran compounds, particularly the correspondingly substituted tetrahydropyran derivatives referred to hereinafter, also fall within the broader aspects of the present invention.

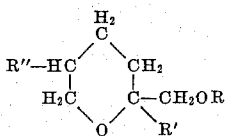
This application relates to subject matter divided from and is a continuation-in-part of my copending application Serial No. 713,455, filed December 2, 1946, Cyclic Organic Compounds, now U. S. Patent No. 2,479,283, issuing August 16, 1949.

The present application relates particularly to dihydropyran compounds having an oxymethyl group and a hydrocarbyl group directly substituted on the carbon atom in the No. 2 position of the dihydropyran ring and corresponding in structure to the structural formula



Formula I

in which R represents a member of the class consisting of hydrogen, hydrocarbyl and acyl, R' represents hydrocarbyl and R'' represents one of the class consisting of hydrogen and hydrocarbyl. Substituted tetrahydropyran derivatives to which the invention relates in its generic aspects correspond in structure to the structural formula



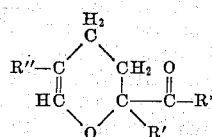
Formula II

in which R, R' and R'' have their above significance. Reference will be made hereinafter to a number of specific compounds falling within the generic class of compounds provided by the present invention. Certain of the preferred mem-

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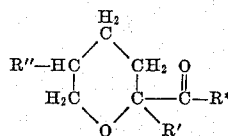
bers of the class may be mentioned individually here; namely the dihydropyran derivatives 2,5-dimethyl-3,4-dihydro-1,2-pyran-2-methanol, 2-methyl-3,4-dihydro-1,2-pyran-2-methanol, and 2,5-dineopentyl-3,4-dihydro-1,2-pyran-2-methanol. As preferred compounds represented when R in the foregoing structural formulas represents acyl there may be particularly mentioned esters of lower alpha,alpha-olefinic carboxylic acids, especially the esters of acrylic and methacrylic acids with the dihydropyran methanols represented when R' and R'' represent lower alkyl groups, such as methyl or ethyl.

In the parent application acknowledged hereinabove, there are disclosed and claimed dihydropyran carbonylic compounds which may be characterized generically as having structures corresponding to the structural formula



Formula III

and tetrahydropyran carbonylic compounds corresponding in structure to the formula



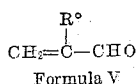
Formula IV

in which formulas R* represents a member of the class consisting of hydrogen, hydroxy, metal-oxo and hydrocarbyloxy, R' represents hydrocarbyl, and R'' represents a member of the class consisting of hydrogen and hydrocarbyl.

In accordance with the inventions claimed in the aforesaid parent application and in the present application, it has been discovered unexpectedly that compounds of the present class may be prepared in a highly efficient and effective manner by means of a process which comprises condensing at a suitable elevated temperature and in the presence of a suitable polymerization inhibitor an alpha,beta-unsaturated aldehyde having attached to the alpha carbon atom a hydrocarbyl group linked to said alpha carbon atom via a single bond. Products which may be prepared by such condensation of alpha,beta-olefinic aldehydes substituted on the alpha carbon atom by a hydrocarbyl group comprise compounds having structures defined by Formula III,

when R* signifies hydrogen and R' and R'' have the significance set forth above. It was in many respects a surprising discovery to find that alpha,beta-unsaturated aldehydes of the present class could be caused to condense to form heterocyclic compounds of the indicated structure. It is known, for example, that many of the reactions of alpha,beta-unsaturated aldehydes are markedly favored by, and in some cases completely dependent upon, the presence of a substitutable hydrogen atom in the alpha position relative to the carbonyl group. It would not normally have been expected that alpha,beta-unsaturated aliphatic aldehydes having no hydrogen atom directly attached to the alpha carbon atom would readily undergo condensation reactions of the type of reaction here involved. Unexpectedly, it has been discovered that the alpha,beta-unsaturated aldehydes of the present class not only undergo such condensation reaction in the presence of a polymerization inhibitor, such as hydroquinone, and at an elevated temperature, but that such reaction may be effected with considerably greater yield of dihydropyran carbonylic compounds, and with greater efficiency and economy of operation, than have been attained in the case of certain related alpha,beta-unsaturated aldehydes heretofore employed. The products that may be prepared by a process comprising such condensation of the present class of alpha,beta-unsaturated aldehydes possess unique and unexpected properties that distinguish them in several respects from compounds heretofore known, and that render them of corresponding advantage in the arts.

The unsaturated aldehydes which may be employed in accordance with the process of the present invention for the production of valuable new oxymethyl-substituted dihydropyran compounds are those unsaturated aldehydes that have an olefinic bond in the alpha, beta position relative to the carbonyl group and that have attached to the alpha carbon atom a singly bonded hydrocarbyl group. The advantages of the invention are most effectively realized by application in the process of those unsaturated aldehydes having structures corresponding to the formula



wherein R* signifies a hydrocarbyl group. The hydrocarbyl group may be either an open chain hydrocarbon group or a cyclic group, such as a cyclic non-aromatic hydrocarbon group or an aromatic hydrocarbon group. It is particularly preferred to employ those aldehydes wherein the hydrocarbon group substituted on the alpha carbon atom is an alkyl group, preferably one containing from one to 10 carbon atoms inclusive.

Representative unsaturated aldehydes which may be employed according to the invention for the preparation of the novel compounds of the invention include the alpha-alkyl acroleins, such as alpha-methylacrolein, alpha-ethylacrolein, alpha-propylacrolein, alpha-isopropylacrolein, the alpha-butylacroleins, the alpha-pentylacroleins, the alpha-hexylacroleins, the alpha-heptylacroleins, and homologous and analogous unsaturated aldehydes having an alkyl group attached to the carbon atom in the alpha position. Although there may be employed unsaturated aldehydes corresponding to the immediately foregoing formula when R* signifies an open

chain or a cyclic hydrocarbon group containing one or more olefinic bonds, most desirably the group represented by R* is one not readily hydrogenated, i. e., a saturated hydrocarbon group or an aromatic group. Cyclic groups which may be represented by R* may be either saturated cycloaliphatic or aromatic in character or less desirably cyclo-olefinic in character. Representative unsaturated aldehydes corresponding to the foregoing formula and containing a cycloaliphatic group are alpha-cyclopentylacrolein, alpha-cyclohexylacrolein, alpha-(2-ethylcyclohexyl)acrolein, alpha-(3-cyclohexylpropyl)acrolein, and homologs and analogs thereof. As unsaturated aldehydes containing an aromatic group there may be mentioned, for example, alpha-phenylacrolein, alpha-tolylacrolein, alpha-benzylacrolein, alpha-(2-phenylethyl)acrolein and homologs and analogs thereof corresponding to the immediately foregoing structural formula.

The hydrocarbon group that may be represented by R* in the foregoing formula may be either substituted or unsubstituted provided the substituent groups thereon, if any, are non-reactive under the conditions employed in the present process and are not in a position in the molecule such that they would affect unfavorably the reactivity of the molecule as a whole in its application in the present process. Substituent groups which thus may be present include, for example, halogen, carbonitrile, ethereal oxygen, etc.

When a single unsaturated aldehyde of the foregoing class is employed in the process of the invention, the product obtained by condensation thereof is a dihydropyran compound corresponding in structure to structural Formula III, when R' and R'' represent the same substituent grouping, i. e., both R and R' represent the same hydrocarbyl group, and R* represents the hydrogen atom. When there is employed instead of a single unsaturated aldehyde of the foregoing formula a mixture of two or more unsaturated aldehydes having structures represented by the formula, there are obtained compounds corresponding in structure to Formula III, when R' and R'' represent different substituent groups within the defined classes of substituent groups, R* again representing hydrogen. When, instead of a mixture of two or more aldehydes corresponding to the foregoing formula, there is employed a mixture comprising, for example, acrolein and an aldehyde of the foregoing formula, there are obtained in excellent yields compounds corresponding in structure to Formula III, when R' and R'' again represent different groups or atoms but one of R' and R'' represents hydrogen. In this case, R* again represents hydrogen. The condensation according to the process of dissimilar alpha,beta-unsaturated aldehydes, at least one of which corresponds in structure to Formula V, provides a highly efficient method of preparing numerous derivatives of dihydropyran and tetrahydropyran that could have been prepared heretofore only by complex and less efficient processes that would not be practicable for application, say on a commercial scale.

Dissimilar alpha,beta-unsaturated aldehydes which may be employed together include, for example, alpha-ethylacrolein and acrolein, alpha-ethylacrolein and methacrolein, alpha-phenylacrolein and alpha-hexylacrolein, and like pairs wherein at least one of the aldehydes is a member of the hereinbefore defined class of unsaturated

aldehydes. Although highly advantageous results may be obtained when acrolein is employed as the second unsaturated aldehyde, it is preferred that both of the unsaturated aldehydes be members of the herein defined class.

According to the process of the present invention, one or a mixture of a plurality of unsaturated aldehydes as defined above is condensed at an elevated temperature in the presence of a suitable polymerization inhibitor to produce dihydropyran compounds corresponding to Formula III, when R* represents hydrogen. As the polymerization inhibitor, there may be employed any suitable compound or material of the class known to the art as anti-oxidants or polymerization inhibitors, which is inert under the existing conditions with respect to reaction with the unsaturated aldehyde or aldehydes and the products of the condensation reaction. Polymerization inhibitors which may be employed according to the invention include, for example, quinones, amines, phenolic compounds, nitro-aryl compounds, mercaptans, and the like. Hydroquinone is highly effective. Compounds which may be employed in place of hydroquinone include benzoquinone, naphthoquinone, phenol, the cresols, a naphthol, a xylenol, thymol, catechol, eugenol, resorcinol, pyrogallol, orcinol, guaiacol, nitrobenzene, dinitrobenzene, a nitrophenol, a nitrosophenol or the like. Inorganic inhibitors which may be employed include, for instance, halogens, copper and alloys thereof, sulfur, selenium, and tellurium. Inorganic elements such as the foregoing also may be present in combined form in organic molecules, as in polysulfides, thioacids, selenoacids, etc.

The amount of polymerization inhibitor that is employed is a minor amount sufficient to inhibit or to prevent the formation of higher polymeric products of reaction under the conditions of reaction. The exact amount that is most suitable depends upon the particular polymerization inhibitor employed, the conditions under which the reaction is effected, the particular reactants involved and similar factors. Frequently, only a trace of polymerization inhibitor is necessary. Generally speaking, amounts of polymerization inhibitor of from about 0.01 to about 10% by weight of the unsaturated aldehyde or aldehydes are effective. Amounts of hydroquinone, for example, of from about 0.025 to about 2% are particularly effective.

The condensation of the unsaturated aldehyde may be effected in the presence of a suitable inert organic solvent, if desired, although particularly advantageous results have been obtained by conducting the condensation in the absence of any added solvent. As the solvent, there may be employed an aromatic hydrocarbon, such as benzene, toluene, xylene, ethylbenzene, or mixtures of aromatic hydrocarbons; an aliphatic hydrocarbon such as octane, a nonane, or other aliphatic hydrocarbons that are liquid under the conditions employed; an ether, such as diethyl ether, dipropyl ether, diisooamyl ether; a heterocyclic compound, such as dioxane, furan, etc.; and the like. Mixtures of solvents may be employed if desired. Benzene is particularly satisfactory as the solvent if one is employed. There may be employed up to about 10 parts of solvent per part of aldehyde, preferably up to about 2 parts of solvent per part of aldehyde.

Dihydropyran carboxaldehydes according to Formula III may be prepared by heating the olefinic aliphatic aldehyde of the present class,

or mixture of olefinic aldehydes comprising an aldehyde of the present class, at an elevated temperature under sufficient pressure to maintain the reaction mixture in the liquid state.

Temperatures of from about 50° C. to about 240° C. may be used, in general, although at times either somewhat higher or somewhat lower temperatures may be employed satisfactorily. The preferred range of temperature depends in part upon the particular unsaturated aldehyde used. Temperatures from about 100° C. to about 240° C., preferably from about 140° C. to about 200° C., generally are employed. Temperatures sufficiently high to promote excessive decomposition of reactants or reaction products should be avoided. The reaction preferably is effected under superatmospheric pressure, although with higher boiling reactants and reaction products, atmospheric or lower pressures may be employed. In any case, however, the pressure is maintained at or above the total vapor pressure of the reaction mixture at the temperature of reaction. Pressures sufficient to maintain the liquid state and from atmospheric pressure up to about 3000 pounds per square inch thus may be employed. Preferably, the pressure is maintained between about 500 pounds per square inch and about 2000 pounds per square inch. If superatmospheric, the pressure conveniently may be autogenous as in a closed reaction vessel, or it may be applied by introduction of a suitable inert gas such as nitrogen, carbon dioxide, methane, ethane, propane, etc., into the reaction vessel. Oxygen desirably is excluded from the reaction vessel.

The reaction time may be varied over relatively wide limits. Higher temperatures of reaction generally enable the use of shorter reaction times. Reaction times of from about ¼ hour or less to 24 hours or more have been employed. Under the optimum conditions of reaction, satisfactory completion of the reaction ordinarily is obtained with a reaction time of from about ¼ hour to about 2 hours.

The process of the invention may be executed either batchwise, intermittently, or continuously. For batchwise operation, the polymerization inhibitor and the organic solvent, if one is employed, may be mixed with the unsaturated aldehyde reactant or reactants, and the resultant mixture heated to a suitable temperature and under pressure adequate to maintain the liquid phase, for a time sufficient to complete the reaction. The reaction preferably is carried out in a reaction vessel which may be either glass-lined or constructed of stainless steel, iron, carbon-steel, or alloys of metals such as copper, nickel, chromium, etc. A glass-lined reaction vessel generally is preferable because of possible catalytic effects of metallic impurities in promoting side-reactions, extensive polymerization, etc. In continuous operations, particular advantages are realized by effecting the reaction in the absence of any added organic solvent. A continuous stream of the unsaturated aldehyde or mixture of unsaturated aldehydes containing the polymerization inhibitor may be passed through a reaction zone such as an elongated reaction tube maintained at a temperature within the range of suitable reaction temperatures, the dimensions of the tube and the rate of flow of the reactant stream being so correlated as to obtain adequate residence time of the reaction mixture at the reaction temperature. It will be appreciated, however, that the process is not limited according to the particular ap-

paratus that is employed, and a wide variety of equipment apparent to those skilled in the art may be used with advantageous results.

After completion of the reaction, the substituted dihydropyran-2-carboxaldehydes provided thereby may be recovered from the reaction mixture in any suitable way desired. Fractional distillation under reduced pressure is eminently satisfactory as a method of recovery. Other methods, such as treatment with selective solvents, may be employed. If desired, any unreacted aldehyde or aldehydes may be separated from the reaction mixture and recycled through the process. The solvent, if one is employed, likewise may be reused. As recovered, at least those products formed from the lower molecular weight unsaturated aldehydes are liquid, high-boiling materials. They may be further purified, if desired, by redistillation or by any other suitable means either chemical or physical.

Products which may be prepared according to the present process from a single unsaturated aldehyde of the herein defined class comprise those compounds having apparent structures defined by Formula III when R* signifies hydrogen and R' and R'' both represent for example, methyl, ethyl, propyl, isopropyl, butyl, hexyl, or the like, or cyclic groups such as phenyl, xylyl, tolyl, cyclohexyl, cyclopentyl, phenethyl, cyclohexylmethyl, methylcyclohexyl, 2-cyclohexylpropyl, or homologous or analogous groups.

When two unsaturated aldehydes are employed in the present process, there may be obtained products comprising substituted dihydropyran carboxaldehydes corresponding in apparent structure to Formula III when R' and R'' differ from each other. For example, when an aldehyde of the present class is reacted with acrolein, there may be obtained as products compounds corresponding in apparent structure to Formula III when one of R' and R'' represents hydrogen and the other represents, for example, methyl as in the products prepared by reaction of methacrolein with acrolein, ethyl as in the products prepared by reaction of alpha-ethylacrolein with acrolein, and the like. When, as in a preferred case, there are employed two unsaturated aldehydes both of which are of the hereinafter defined class, there may be obtained as products dihydropyran carboxaldehydes corresponding in apparent structure to Formula III when R' and R'' both represent hydrocarbonyl but differ from each other. Representative of these products are the compounds wherein R' and R'' represent, both respectively and inversely, methyl and ethyl as in the reaction products of methacrolein and ethacrolein, methyl and isopropyl as in the reaction products of methacrolein and alpha-isopropylacrolein, and analogous products of the reaction of analogous pairs of aldehydes of the present class. Mixtures of more than two aldehydes comprising at least one aldehyde of the present class of aldehydes may be employed, if desired, although preferably a maximum of two aldehydes is employed in order to facilitate separation and/or recovery of any products that may be desired in a relatively pure form.

It unexpectedly has been discovered in accordance with the present invention that substituted dihydropyran aldehydes corresponding in structure to Formula III may be converted to substituted dihydropyran oxymethyl compounds represented by Formula I by treatment of the substituted dihydropyran aldehydes corresponding to Formula III with a strong alkali, such as a caustic

alkali, to cause intermolecular oxidative-reductive reaction resulting in the formation from two molecules of the dihydropyran aldehyde of one molecule of the corresponding dihydropyran methanol and one molecule of the corresponding dihydropyran carboxylic acid. Ordinarily, yields of the dihydropyran oxymethyl compound in excess of 80% of theory may be obtained. Suitable alkalis which may be employed include, for example, sodium hydroxide, potassium hydroxide, lithium hydroxide, and the like. The desired reaction may be accomplished by treating the dihydropyran carboxaldehyde with the alkali, preferably in the form of a concentrated aqueous solution. There preferably is employed an aqueous solution of a caustic alkali or a mixture of caustic alkalis having a concentration of from about 20% to about 50% by weight. Temperatures of from about 15° C. to about 100° C., preferably from about 40° C. to 80° C., desirably are employed. Amounts of the caustic alkali upwards from about 0.2 mole per mole of the dihydropyran carboxaldehyde may be employed. Preferably there are employed between about 0.5 and about 5 moles of caustic alkali per mole of the dihydropyran carboxaldehyde. Reaction may be effected by mixing the solution of caustic alkali with the dihydropyran carboxaldehyde as by gradually adding the caustic solution to the aldehyde with agitation. The reaction ordinarily will be conducted in a suitable reaction vessel equipped with means for controlling the temperature, such as a jacketed vessel or a vessel equipped with internally located cooling coils. The reaction time required may vary from a few minutes to several hours, depending upon the reactants involved and the conditions of the reaction. When the alkali solution has been slowly added to the dihydropyran carboxaldehyde, the reaction frequently will be substantially completed by the time the alkali has been added.

After completion of the reaction, the oxymethyl dihydropyran compound may be recovered from the reaction mixture according to any appropriate method. Ordinarily it will be separated from the alkali salt of the dihydropyran carboxylic acid formed as a by-product by treatment of the crude reaction mixture with a selective solvent. The crude mixture thus may be treated with water to dissolve the carboxylic acid salt. The oxymethyl dihydropyran compound may be recovered from the water-insoluble residue as by fractional distillation, steam distillation, extraction by treatment with an organic solvent or other suitable methods. The aqueous solution of the alkali salt of the dihydropyran carboxylic acid may be extracted by treatment with an organic solvent to recover any oxymethyl dihydropyran compound dissolved or dispersed therein. In other cases, the crude reaction mixture may be extracted by treatment with a water-immiscible organic solvent, such as a hydrocarbon solvent, to extract the oxymethyl dihydropyran compound and the desired product may be recovered from the extract by suitable methods, such as fractional distillation.

In accordance with the invention, oxymethyl dihydropyran compounds corresponding in structure to Formulas I and II may be prepared by hydrogenation of dihydropyran aldehydes corresponding in structure to Formula III, by treatment with molecular hydrogen in the presence of a hydrogenation catalyst. As the catalyst, any suitable metal or compound of a metal falling within the class known to the art as hydrogenation catalysts, may be employed. Representa-

tive metals and compounds of metals falling within this class are, for example, nickel, iron, cobalt, copper, silver, molybdenum, tungsten, vanadium, platinum, palladium, gold, tin, and the like, and compounds thereof, such as the catalytically active oxides, etc. Mixtures or alloys of suitable metals may be employed as hydrogenation catalysts. Mixtures of suitable compounds of metals may also be employed. It surprisingly has been discovered that the formyl group of the herein-described dihydropyran aldehydes may be preferentially converted to an oxymethyl or methylol group while avoiding substantial saturation of the multiple bond of the heterocyclic ring by conducting the hydrogenation in the presence particularly of base metal hydrogenation catalysts at an elevated temperature and under a superatmospheric pressure of hydrogen. By employing more severe conditions of hydrogenation, that is higher temperatures and higher pressures of hydrogenation, saturation of the heterocyclic ring to produce oxymethyl tetrahydropyran compounds corresponding to Formula II also may be attained. Although the hydrogen pressures may be varied widely, hydrogen pressures of from about 50 pounds per square inch to about 10,000 pounds per square inch ordinarily will be employed, a preferred range being hydrogen pressures of from about 500 pounds per square inch to about 2500 pounds per square inch. Temperatures of from about 20° C. to about 150° C. ordinarily will be employed, although temperatures as high as 250° C. may be operable. For the preparation of dihydropyran oxymethyl compounds according to Formula I, it is particularly preferred to employ a nickel hydrogenation catalyst, such as the well-known Raney nickel catalyst, and to conduct the hydrogenation at temperatures preferably within the range of from about 25° C. to about 75° C. and at hydrogen pressures of from about 500 pounds per square inch to about 2000 pounds per square inch. For the preparation of tetrahydropyran oxymethyl compounds according to Formula II by hydrogenation in the presence of Raney nickel of dihydropyran aldehydes according to Formula III, hydrogen pressures of from about 500 to about 2000 pounds per square inch and temperatures from about 75° C. to about 140° C. are preferred.

The hydrogenation may be effected according to any suitable method, as continuously, intermittently, or batchwise. The material to be hydrogenated may, if desired, be dispersed or dissolved in a suitable organic solvent such as a hydrocarbon, an ether, an alcohol, etc. Amounts of the solvent from about 0.5 part to about 5 parts by weight per part of the dihydropyran aldehyde ordinarily are satisfactory. After completion of the hydrogenation, the catalyst may be removed by filtration or other effective means and the resultant mixture separated into its components by fractional distillation, by treatment with selective solvents, or in other suitable ways.

Tetrahydropyran oxymethyl compounds according to Formula II may be prepared by hydrogenation of corresponding dihydropyran oxymethyl compounds according to Formula I.

Representative substituted dihydropyran methanols embraced within the invention include, among others, the following: 2-methyl-3,4-dihydro-1,2-pyran-2-methanol, 2,5-dimethyl-3,4-dihydro-1,2-pyran-2-methanol, 2-ethyl-3,4-dihydro-1,2-pyran-2-methanol, 2,5-diethyl-3,4-dihydro-1,2-pyran-2-methanol, 2,5-diisopropyl-3,4-dihydro-1,2-pyran-2-methanol, 2-isobutyl-5-eth-

yl-3,4-dihydro-1,2-pyran-2-methanol, 2,5-di-*t*-butyl-3,4-dihydro-1,2-pyran-2-methanol, 2,5-dineopentyl-3,4-dihydro-1,2-pyran-2-methanol, 2,5-diphenyl-3,4-dihydro-1,2-pyran-2-methanol, 2,5-dicyclohexyl-3,4-dihydro-1,2-pyran-2-methanol, 2,5-diocetyl-3,4-dihydro-1,2-pyran-2-methanol, and 2,5-dimethoxyphenyl-3,4-dihydro-1,2-pyran-2-methanol. Particularly valuable and preferred are the substituted 3,4-dihydro-1,2-pyran-2-methanols which are described by Formula I and which contain like lower alkyl substituents in the 2 and 5 positions of the dihydropyran ring.

Corresponding tetrahydropyran oxymethyl compounds are as follows: 2-methyltetrahydropyran-2-methanol, 2,5-dimethyltetrahydropyran-2-methanol, 2-ethyltetrahydropyran-2-methanol, 2,5-diethyltetrahydropyran-2-methanol, 2,5-diisopropyltetrahydropyran-2-methanol, 2-isobutyl-5-ethyltetrahydropyran-2-methanol, 2,5-di-*t*-butyltetrahydropyran-2-methanol, 2,5-dineopentyltetrahydropyran-2-methanol, 2,5-diphenyltetrahydropyran-2-methanol, 2,5-dicyclohexyltetrahydropyran-2-methanol, 2,5-diocetyltetrahydropyran-2-methanol, and 2,5-dimethoxyphenyltetrahydropyran-2-methanol. Particularly valuable are the substituted tetrahydropyran-2-methanols which contain like lower alkyl substituents in the 2 and 5 positions and are represented in structure by Formula II.

Esters of the foregoing and the analogous and homologous dihydropyran and tetrahydropyran methanols with carboxylic or other acids may be prepared according to known procedures, for example, by reaction between the dihydropyran or tetrahydropyran methanol and the acid anhydride, or the acid chloride, the acid anhydride being preferred. The esters of the alcohols of the invention with acids such as acetic acid, propionic acid, butyric acid, caproic acid, lauric acid, stearic acid, benzoic acid, naphthoic acid, acrylic acid, methacrylic acid, crotonic acid, pelargonic acid, octenoic acid, 1,3-butadiene-1-carboxylic acid, oleic acid, succinic acid, adipic acid, glutaric acid, chlorobenzoic acid, beta-ethoxypropionic acid, and like carboxylic acids are included within the invention. For many purposes, the esters in which the acyl radical derived from the carboxylic acid contains, in addition to the carbonyl oxygen atom, only atoms of carbon and of hydrogen are particularly preferred. Representative esters of the invention are: 2,5-dimethyl-3,4-dihydro-1,2-pyran-2-methanol acetate, 2,5-dimethyl-3,4-dihydro-1,2-pyran-2-methanol isobutyrate, 2,5-dimethyl-3,4-dihydro-1,2-pyran-2-methanol acrylate, 2-methyl-3,4-dihydro-1,2-pyran-2-benzoate, 2,5-diethyl-3,4-dihydro-1,2-pyran-2-methanol laurate, 2,5-dimethyl-3,4-dihydro-1,2-pyran-2-methanol phthalate, 2,5-dineopentyl-3,4-dihydro-1,2-pyran-2-methanol oleate, 2,5-dineopentyl-3,4-dihydro-1,2-pyran stearate, 2-methyl-5-ethyl-3,4-dihydro-1,2-pyran crotonate, 2,5-diisopropyl-3,4-dihydro-1,2-pyran-2-methanol furoate, 2-isopropyl-5-butyl-3,4-dihydro-1,2-pyran-2-methanol methacrylate. The corresponding compounds saturated in the pyran ring may be prepared.

Ethers of the novel dihydropyran and tetrahydropyran methanols, which ethers are represented by Formulas I and II, respectively, when R represents a hydrocarbon group which may be substituted, include the ethers with monohydric and dihydric alcohols, such as the methyl, ethyl, propyl, isopropyl, benzyl, cyclohexyl, naphthyl, vinyl, allyl, crotyl, methallyl, 2-ethoxyethyl and

3-hydroxypropyl ethers and homologs and analogs thereof.

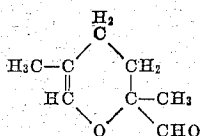
Representative ethers included by the invention are as follows: 2,5-dimethyl-3,4-dihydro-1,2-pyran-2-methyl ethyl ether, 2,5-dimethyl-3,4-dihydro-1,2-pyran-2-methyl propyl ether, 2-methyl-3,4-dihydro-1,2-pyran-2-methyl chloroethyl ether, 2,5-diisopropyl-3,4-dihydro-1,2-pyran-2-methyl ethoxyethyl ether, 2,5-dibutyl-3,4-dihydro-1,2-pyran-2-methyl phenyl ether, 2,5-dimethyl-3,4-dihydro-1,2-pyran-2-methyl naphthyl ether, 2,5-dineopentyl-3,4-dihydro-1,2-pyran-2-methyl allyl ether, 2-methyl-5-ethyl-3,4-dihydro-1,2-pyran-2-methyl methallyl ether and 2,5-dibutyl-3,4-dihydro-1,2-pyran-2-methyl lauryl ether. The corresponding tetrahydropyran ethers may be prepared and are embraced by the generic invention.

The novel heterocyclic alcohols to which the invention relates are of value as special solvents, plasticizers and as chemical intermediates. The alcohols are of interest as raw materials for the preparation of useful amines obtainable by replacement of the hydroxyl group by an amino nitrogen atom which may be, for example, unsubstituted or which may have one or both of the hydrogen atoms replaced by an alkyl, aryl, alkaryl, or olefinic group. Ethers of the new alcohols, for example, with lower monohydric saturated aliphatic alcohols, are of particular interest as special solvents. The ethers with higher alcohols, for example, the ethers with alcohols of the aliphatic type containing from 10 to 18 carbon atoms are of potential value as plasticizers and as softening agents, for example, in the treatment of leather. Esters of the novel alcohols with alpha-methylene carboxylic acids, particularly of the aliphatic type, are useful as resin intermediates from which there may be prepared improved polymers. Esters of the novel alcohols with saturated aliphatic carboxylic acids may be employed as plasticizers, as special solvents, and as chemical intermediates.

The following examples will serve to illustrate certain specific embodiments of the present invention.

Example I

Preparation of 2,5-dimethyl-3,4-dihydro-1,2-pyran-2-carboxaldehyde.—Methacrolein containing 1% by weight of added hydroquinone was dissolved in an equal weight of benzene and the solution was heated at 170° C. for 3 hours under the autogenous pressure in a glass lined reaction vessel. Upon fractional distillation of the resulting mixture, 2,5-dimethyl-3,4-dihydro-1,2-pyran-2-carboxaldehyde was recovered as a fraction boiling at 101° C. to 101.4° C. under a pressure of 90 millimeters of mercury. Conversion, 77%, yield, 94%. The product was found to have a refractive index (n_D^{20}) of 1.4537. It was found to contain 68.43% carbon and 8.66% hydrogen compared to theoretical values of 68.54% carbon and 8.63% hydrogen. The structure formula for 2,5-dimethyl-3,4-dihydro-1,2-pyran-2-carboxaldehyde is

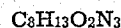


The compound which is referred to as 2,5-dimethyl-3,4-dihydro-1,2-pyran-2-carboxaldehyde

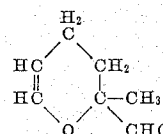
may also be named as 2,5-dimethyl-2-formyl-2,3-dihydropyran.

Example II

Preparation of 2-methyl-3,4-dihydro-1,2-pyran-2-carboxaldehyde.—A mixture of 1700 parts of methacrolein and acrolein present in a 1:2.6 molar ratio containing 1% of hydroquinone was passed in a continuous stream through a stainless steel tube having a free space of 185 cubic centimeters at a flow rate of 1.85 volumes of feed per hour per volume under a pressure of 620 to 720 pounds per square inch. Prior to introduction into the reactor, the stream was preheated to 210° C. and a reactor temperature of 210° C. was maintained by externally located electrical heaters. The reactor effluent was collected and distilled. A fraction boiling between 78° C. at 90 millimeters mercury pressure and 58.4° C. at 16 millimeters mercury pressure was separated in the amount of 502 parts. By redistillation of this fraction there was obtained 330 parts of 2-methyl-3,4-dihydro-1,2-pyran-2-carboxaldehyde boiling at 84.4° C. to 85.5° C. under a pressure of 90 millimeters of mercury and having a refractive index of 1.455 to 1.456. The semicarbazone of the 2-methyl-3,4-dihydro-1,2-pyran-2-carboxaldehyde was prepared and after recrystallization was found to contain 22.3% nitrogen and 51.9% carbon. Theory for

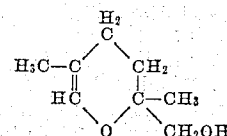


22.9% nitrogen and 52.4 carbon. The structural formula for 2-methyl-3,4-dihydro-1,2-pyran-2-carboxaldehyde is



Example III

Preparation of 2,5-dimethyl-3,4-dihydro-1,2-pyran-2-methanol.—One hundred seventy-nine parts of sodium hydroxide in the form of a 40% aqueous solution was added in 1/2 hour to 300 parts of 2,5-dimethyl-3,4-dihydro-1,2-pyran-2-carboxaldehyde while the mixture was held by cooling at 40–50° C. The nearly solid resulting mixture was diluted with 300 parts of water and extracted with portions of diethyl ether totalling 1000 parts. The combined ether extract was dried and distilled. After separation of the ether, 130 parts of 2,5-dimethyl-3,4-dihydro-1,2-pyran-2-methanol distilling at 75.8–79.6° C. under a pressure of 7–8 millimeters of mercury were recovered. The refractive index of the 2,5-dimethyl-3,4-dihydro-1,2-pyran-2-methanol was found to be 1.4733. The product was found to contain 67.53% carbon and 9.90% hydrogen compared to calculated values of 67.57% carbon and 9.92% hydrogen. The structural formula for 2,5-dimethyl-3,4-dihydro-1,2-pyran-2-methanol is



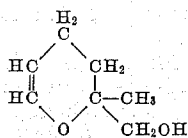
The compound which is referred to as 2,5-dimethyl-3,4-dihydro-1,2-pyran-2-methanol may also be assigned the name 2,5-dimethyl-2-hydroxymethyl-2,3-dihydropyran.

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The aqueous solution remaining after the extraction with ether contained the sodium salt of 2,5-dimethyl-3,4-dihydro-1,2-pyran-2-carboxylic acid. The free acid can be recovered by acidification of the solution, extraction of the acidified solution with diethyl ether, and evaporation of the ether from the extract.

Example IV

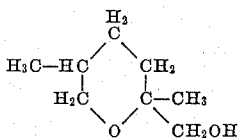
Preparation of 2-methyl-3,4-dihydro-1,2-pyran-2-methanol.—2-methyl-3,4-dihydro-1,2-pyran-2-carboxaldehyde was treated with sodium hydroxide according to the method of Example III. 2-methyl-3,4-dihydro-1,2-pyran-2-methanol was separated from the resulting mixture by extraction with diethyl ether and distillation of the dried extract. 2-methyl-3,4-dihydro-1,2-pyran-2-methanol was found to have a boiling point of 75° C. under 10 millimeters mercury pressure and a refractive index of 1.4752. Analysis verified the empirical formula $C_7H_{12}O_2$ for the product. The structural formula for 2-methyl-3,4-dihydro-1,2-pyran-2-methanol is



2-methyl-3,4-dihydro-1,2-pyran-2-carboxylic acid can be recovered from the extract alkaline solution according to the method described in the preceding example.

Example V

Preparation of 2,5-dimethyltetrahydropyran-2-methanol.—To 187 parts of 2,5-dimethyl-3,4-dihydro-1,2-pyran-2-carboxaldehyde there were added 10 parts of Raney nickel catalyst. The mixture was hydrogenated by treatment with molecular hydrogen under a pressure of 800 to 1700 pounds per square inch at a temperature of 100° C. to 125° C. After 22 hours no further hydrogen was absorbed. The catalyst was removed by filtration and the filtrate distilled in vacuo. There were obtained 156.5 parts of 2,5-dimethyltetrahydropyran-2-methanol distilling at 82.8–83.6° C. under 10 millimeters mercury pressure. The product was found to contain 66.57% carbon, 11.20% hydrogen and to have a hydroxyl titre of 0.688 equivalent per 100 grams compared to calculated values of 66.63% carbon, 11.18% hydrogen and 0.694 equivalent of hydroxyl per 100 grams. The structural formula for 2,5-dimethyltetrahydro-2-methanol is



Example VI

Preparation of 2,5-dimethyl-3,4-dihydro-1,2-pyran-2-methanol and 2,5-dimethyltetrahydropyran-2-methanol.—One mole of 2,5-dimethyl-3,4-dihydro-1,2-pyran-2-carboxaldehyde was treated with hydrogen under a pressure of 1000 pounds per square inch at 25° C. to 55° C. for 14 hours in the presence of 10% by weight of Raney nickel catalyst. The products of the hydrogenation were separated by distillation of the filtered mixture. 2,5-dimethyl-3,4-dihydro-1,2-pyran-2-methanol and 2,5-dimethyltetrahydropyran-2-methanol were obtained.

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Example VII

2-methyl-3,4-dihydro-1,2-pyran-2-methanol acetate.—2-methyl-3,4-dihydro-1,2-pyran-2-methanol acetate, which may be prepared by esterification of 2-methyl-3,4-dihydro-1,2-pyran-2-methanol by treatment with, for example, acetic anhydride, has been prepared and found to have the following characteristics:

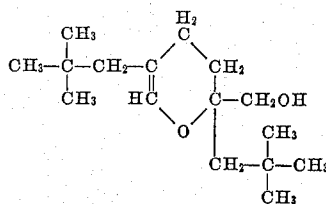
Boiling point (1 millimeter mercury pressure) -----	°C. 60–63
Refractive index (n_D^{20}) -----	1.457
Specific gravity (20/4) -----	1.049

Example VIII

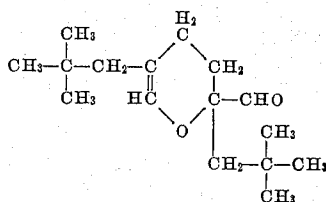
Preparation of 2,5-dineopentyl-3,4-dihydro-1,2-pyran-2-carboxaldehyde.—Alpha-neopentyl acrolein was condensed according to the method illustrated in Examples I and II by heating in a stainless steel bomb for one hour at 165–190° C. Crude 2,5-dineopentyl-3,4-dihydro-1,2-pyran-2-carboxaldehyde was recovered by rapid distillation of the resulting mixture with collection of the fraction distilling between 98° C. and 110° C. at about 1 millimeter of mercury pressure. By redistillation of this fraction there was obtained purified 2,5-dineopentyl-3,4-dihydro-1,2-pyran-2-carboxaldehyde distilling at 91.4–91.6° C. under a maximum pressure of 1 millimeter of mercury. Analyses of the purified product were as follows: 76.1% carbon, 11.2% hydrogen and 0.41 equivalent carbonyl per 100 grams were found compared to calculated values of 76.2% carbon, 11.2% hydrogen and 0.40 equivalent carbonyl per 100 grams.

Example IX

Preparation of 2,5-dineopentyl-3,4-dihydro-1,2-pyran-2-methanol.—Ninety-two parts of 2,5-dineopentyl-3,4-dihydro-1,2-pyran-2-carboxaldehyde were dissolved in 100 parts of methanol and placed with 9 parts of Raney nickel hydrogenation catalyst in a hydrogenation bomb. The mixture was hydrogenated at 125° C. under 700 to 1200 pounds per square inch hydrogen pressure. Distillation of the filtered solution led to the separation of 36 parts of product distilling at 130–135° C. under 2 millimeters mercury pressure. 2,5-dineopentyl-3,4-dihydro-1,2-pyran-2-methanol has the structure



The structural formula of 2,5-dineopentyl-3,4-dihydro-1,2-pyran-2-carboxaldehyde is

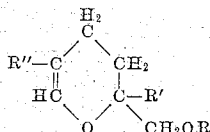


The claimed invention is:

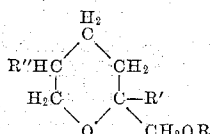
1. As a new chemical compound, a member of the class consisting of (1) the dihydropyran de-

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rivatives having structures corresponding to the formula

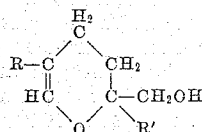


when R represents one of the class consisting of hydrogen, hydrocarbyl, and acyl residues of carboxylic acids, R' represents hydrocarbyl, and R'' represents one of the class consisting of hydrogen and hydrocarbyl, and (2) the tetrahydropyran derivatives having structures corresponding to the formula



when R represents one of the class consisting of hydrogen, hydrocarbyl, and acyl residues of carboxylic acids, R' represents hydrocarbyl, and R'' represents one of the class consisting of hydrogen and hydrocarbyl.

2. As new chemical compounds dihydropyran derivatives having structures corresponding to the formula



in which R and R' represent like alkyl groups.

3. 2,5-dimethyl-3,4-dihydro-1,2-pyran-2-methanol.

4. 2,5-dimethyltetrahydropyran-2-methanol.

5. 2,5-dialkyltetrahydropyran-2-methanol.

6. An ester of an unsubstituted aliphatic monocarboxylic acid and a 2,5-dialkyltetrahydropyran-2-methanol.

7. An ester of an unsubstituted aliphatic carboxylic acid and a 2,5-dialkyl-3,4-dihydro-1,2-pyran-2-methanol.

8. An ester of an unsubstituted aliphatic carboxylic acid and 2,5-dimethyl-3,4-dihydro-1,2-pyran-2-methanol.

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9. An ester of an unsubstituted aliphatic carboxylic acid and 2,5-dimethyltetrahydropyran-2-methanol.

10. The process of preparing 2,5-dimethyl-2-hydroxymethyl-2,3-dihydropyran which comprises reacting one mole of 2,5-dimethyl-2-formyl-2,3-dihydropyran with one mole of hydrogen in the presence of a hydrogenation catalyst.

11. The process of claim 10 in which the catalyst is a copper-containing hydrogenation catalyst.

12. The process of claim 10 in which the catalyst is a nickel hydrogenation catalyst.

13. A process for the preparation of 2,5-dimethyl-3,4-dihydro-1,2-pyran-2-methanol by hydrogenation of 2,5-dimethyl-3,4-dihydro-1,2-pyran-2-carboxaldehyde which comprises hydrogenating said 2,5-dimethyl-3,4-dihydro-1,2-pyran-2-carboxaldehyde by treatment with hydrogen gas at a pressure of from about 500 pounds per square inch to about 10,000 pounds per square inch at a temperature from about 20° C. to about 150° C. in the presence of Raney nickel hydrogenation catalyst.

14. A process for the preparation of a 2,5-dialkyl-3,4-dihydro-1,2-pyran-2-methanol which comprises reacting one mole of a 2,5-dialkyl-3,4-dihydro-1,2-pyran-2-carboxaldehyde with one mole of hydrogen in the presence of a hydrogenation catalyst.

15. The process of claim 14 in which the catalyst is a copper-containing hydrogenation catalyst.

16. The process of claim 14 in which the catalyst is a nickel hydrogenation catalyst.

RICHARD R. WHETSTONE.

REFERENCES CITED

The following references are of record in the file of this patent:

FOREIGN PATENTS

Number	Country	Date
913,941	France	June 11, 1946