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CONVERTING ALPHA-PINENE TO MIXTURES OF ACIDS

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4 Claims. (Cl. 260—514)

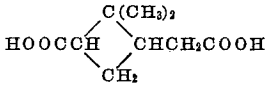
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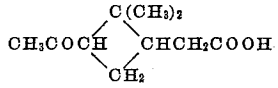
This invention relates to the acids which can be derived by oxidizing alpha-pinene until one or more carboxyl groups are formed on the hydrocarbon structure without opening the substituted cyclobutane ring. Such acids will hereinafter be referred to as "pinene-derived" acids. More particularly, the invention provides: unique and valuable mixtures of hydrocarbon dicarboxylic pinene-derived acids, and mixtures of keto-substituted monocarboxylic pinene-derived acids; and a process for the preparation of such mixtures of acids.

The "pinene-derived" acids consist essentially of acids having the following structural formulas:

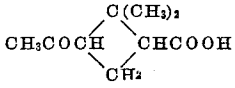
The pinic acids,



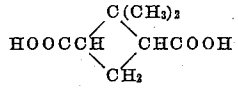
the pinonic acids,



the pinononic acids



and the norpinic acids



There are a plurality of sterio isomers having each of the above structural formulas. Although the proportions may vary widely, substantially all of the pinene-derived acids are produced concurrently when alpha-pinene is oxidized. The chemical relationship between many of the pinene-derived acids is so close that a complete separation of one individual pinene-derived acid is not commercially feasible by proven large-scale separation processes.

An object of the present invention is the provision of a process for converting alpha-pinene to the pinene-derived acids mixed in such proportions that a commercially feasible separation procedure, which isolates groups of acids of like physical and chemical properties, isolates from the mixture produced by said conversion: mixtures of hydrocarbon dicarboxylic pinene-derived acids predominating in pinic and norpinic acids, containing minor amounts of other pinene-derived acids constituting a uniquely valuable mixture of acids; and mixtures of keto-substituted monocarboxylic pinene-derived acids predominating in pinonic and pinononic acids, containing minor amounts of other pinene-derived acids, and constituting a uniquely valuable mixture of acids.

Another object of the present invention is the provision of a commercially feasible process of producing pinene-derived acids, which process, by consuming only comparatively low cost reagents and by avoiding the production of possibly explosive materials in a form in which they could be explosive, avoids the disadvantages inherent in the processes heretofore developed. A further object of the invention is the provision of an ozonolysis process which can be controlled to produce mixtures of the pinene-derived acids predominating in hydrocarbon dicarboxylic pinene-derived acids or predominating in keto-substituted monocarboxylic pinene-derived acids. A further object is to provide mixtures of acids containing acyl radicals which impart unique and valuable properties to mixtures of derivatives produced by the acid reactions of the mixtures of acids. Further objects and advantages of the invention will be apparent to those skilled in the art.

It has been known for over 50 years that the pinene-derived acids could be produced by an alkaline potassium permanganate oxidation. However, as it is well recognized, a large-scale production of a chemical material by a permanganate oxidation process is generally far too expensive to be commercially feasible.

It is also known that the pinene-derived acids can be produced by ozonizing alpha-pinene and decomposing the ozonides into the acids. However, the ozonides of alpha-pinene are insoluble in alpha-pinene in turpentine and in hydrocarbons generally, and also in halo-hydrocarbons generally. As is well known, undiluted ozonides are dangerous because they often become explosively reactive under ordinary conditions of temperature and pressure. Therefore, while ozonization processes which involve an ozonization of alpha-pinene in the vapor-phase, or in carbon tetrachloride, or in hexane, or in chloroform, have been reported, such processes inherently involve the production of considerable quantities of undiluted ozonides, a possibly dangerous material.

We have discovered that alpha-pinene can be converted to pinene-derived acids by an ozonolysis process in which no undiluted ozonides are formed, if, in the process, the alpha-pinene is ozonized while mixed with a "liquid ozonolysis medium" in which the ozonides of alpha-pinene are appreciably soluble. We have discovered that when an ozone-containing gas is passed, in accordance with a conventional procedure for the ozonization of a liquid, into a mixture of alpha-pinene and such a medium at a temperature between the freezing temperature of the solution of alpha-pinene in said medium and the temperature at which ozonides of alpha-pinene dissolved in said medium decompose at an uncontrollably rapid rate, the ozonization reaction produces ozonides of alpha-pinene dissolved in said medium rather than producing a separate phase consisting essentially of ozonides. We have discovered that certain alkanols, alkanoic acids, nitroalkanes, alkanediols and mixtures thereof not only constitute liquid ozonolysis mediums in which alpha-pinene can be so ozonized, but also constitute mediums in which the ozonides so produced can be decomposed into the pinene-derived acids by a homogeneous liquid-phase reaction with an "ozonide-decomposing reagent." We have discovered that certain liquids such as acetic acid, nitromethane and liquid alkanol solutions containing dissolved aqueous alkali metal hydroxides not only constitute liquid ozonolysis mediums in which alpha-pinene can be so ozonized but also constitute ozonide-decomposing reagents in which the dissolved ozonides can be caused to undergo decomposition into the pinene-derived acids at a controllable rate by raising the temperature of the solution. We have also discovered that such a conversion of alpha-pinene can be controlled to favor the production of hy-

drocarbon dicarboxylic or keto-substituted monocarboxylic pinene-derived acids by dissolving in the liquid phase containing the ozonides, during or following the decomposition of the ozonides with an oxonide-decomposing reagent, an "ozonide-decomposition-controlling reagent" such as hydrogen peroxide, water-soluble inorganic peroxides, or a water-soluble mixture of salts of the hypohalous acids with excess inorganic base.

The process of producing pinene-derived acids, provided by this invention, comprises: mixing alpha-pinene with a liquid ozonolysis medium; contacting the mixture with an ozone-containing gas; and subjecting the dissolved ozonides so produced to an acid-producing ozonide decomposition.

Throughout the remainder of the specification, and in the claims: the term "liquid ozonolysis medium" refers to a material which is a homogeneous liquid at atmospheric temperatures and pressures, which consists of one or a plurality of substances, which is appreciably miscible (miscible with at least 0.05 part by weight) with alpha-pinene and the ozonides of alpha-pinene, and which is substantially unreactive towards ozone at a temperature between the temperature at which a solution of alpha-pinene in said material freezes and the temperature at which the ozonides of alpha-pinene dissolved in said material undergo an uncontrollably rapid decomposition; the term "ozonide-decomposing reagent" refers to a substance which is composed of one or more compounds, which reacts with the ozonides of alpha-pinene to produce one or more pinene-derived acids, which is sufficiently miscible with a liquid ozonolysis medium (at least in the presence of an unreactive mutual solvent) to so react with the ozonides in a homogeneous liquid phase containing the ozonides at a temperature between the freezing temperature of the solution of ozonides in the liquid ozonolysis medium and the temperature at which the ozonides dissolved in the liquid ozonolysis medium undergo a thermal decomposition; the term "ozonide-decomposition-controlling reagent" refers to a substance which is composed of one or more compounds, which reacts with a portion of the decomposing ozonides of alpha-pinene or with a portion of the pinene-derived acids to produce hydrocarbon dicarboxylic pinene-derived acids or to produce keto-substituted monocarboxylic pinene-derived acids between the temperatures at which a solution of alpha-pinene ozonides in a liquid ozonolysis medium freezes and boils under atmospheric pressure.

A preferred method of conducting the process of this invention comprises: mixing alpha-pinene with from 2 to 10 parts of methanol; ozonizing the solution so produced at a temperature between the freezing temperature of the solution and the uncontrollably rapid decomposition temperature of the dissolved ozonides of alpha-pinene; and adding, to the solution of ozonides so produced, an amount of sodium hypochlorite providing at least an equivalent of hypochlorite anions based on the amount of ozonides in solution and an amount of sodium hydroxide sufficient to render the solution basic, at a temperature of from 20° to 125° C.

A preferred method of conducting the process comprises: ozonizing alpha-pinene by the above preferred method in which the methanol is replaced by acetic acid; and decomposing the ozonides by diluting the solution of them, so produced, with from 0.1 to 2 parts of water, at a temperature of from 20° to 125° C.

A preferred method of conducting the process comprises: ozonizing alpha-pinene by the above preferred method using acetic acid; and decomposing the ozonides by dissolving in the solution of them, so produced, from 0.1 to 2 parts of water and from 0.01 to 0.03 part of hydrogen peroxide, at from 20° to 125° C.

Where the liquid ozonolysis medium used is completely miscible with alpha-pinene it is preferable to mix the pinene with about 2 to 10 parts of said medium prior to ozonization. Where the liquid ozonolysis medium used is only partially miscible with alpha-pinene up to about 1 part of undissolved alpha-pinene for each part of liquid ozonolysis medium can suitably be present in the reactor at the start of the ozonization.

The miscibility of the ozonide-decomposing reagent and/or the ozonide-decomposition-controlling reagent with the liquid ozonolysis medium can suitably vary widely, and mutual solvents to increase the miscibility of said reagents can suitably be added to the effluent from the ozonization reaction vessel. However, preferred liquid ozonization mediums are those which will dissolve, per part by weight of ozonization medium, at least 0.1 part of alpha-pinene, at least 0.2 part of α-pinene ozonide, at least 0.1 part of ozonide-decomposing reagent, and, if one is to be used, at least 0.02 part of ozonide-decomposition-controlling reagent.

Illustrative examples of liquids which, individually or mixed together, can suitably constitute the liquid ozonization medium used in the process of this invention include: the normally liquid alkanols such as methanol, ethanol, the butanols, the hexanols, the octanols, and the like alcohols; nitromethane; ethylene, propylene, butylene and the like glycols; the thermally stable water-soluble alkanoic acids, i. e. those containing from 2 to about 5 carbon atoms, such as acetic, propionic, isobutyric and the like acids. Methanol and acetic acid are particularly suitable.

Illustrative examples of liquids which, individually or mixed together, can suitably constitute both the liquid ozonolysis medium and the ozonide-decomposing reagent, include: solutions consisting of alkali metal hydroxides dissolved in homogeneous aqueous alkanols which solutions, in the amounts used, contain an amount of base sufficient to neutralize the amount of pinene derived acids obtainable from the amount of alpha-pinene ozonized, e. g., from 0.3 to 1 part of sodium hydroxide in from 50% to 95% aqueous methanol per part of alpha-pinene; nitromethane; and concentrated completely water-miscible alkanoic acids, e. g., aqueous acetice acids of from 50% to 100% acetic acid. Such liquids can suitably be used as ozonolysis mediums for an ozonolysis conducted at a temperature below the decomposition temperature of the dissolved ozonides and subsequently used as ozonide-decomposing reagents by causing the temperature to increase until decomposition occurs. They can also be suitably used as mediums in which both the formation of the ozonide and the acid-producing decomposition of the ozonide occurs concurrently by conducting the ozonization at some higher temperature below the temperature at which the rate of decomposition of the dissolved ozonides becomes uncontrollably rapid.

Illustrative examples of suitable ozonide-decomposing reagents, include: water-soluble organic acids such as the alkanoic acids of from 2 to 5 carbon atoms, the inorganic strong acids such as nitric, hydrochloric, perchloric, sulfuric, phosphoric and the like acids, and the water-soluble inorganic bases such as the hydroxides of the alkali metals and the like bases. Acetic acid and sodium hydroxide are particularly suitable. The ozonide-decomposing reagents are preferably added in increments in the form of an aqueous solution containing one or more of such reagents.

Illustrative examples of suitable ozonide-decomposition-controlling reagents, include: water-soluble inorganic peroxides such as hydrogen peroxide, sodium peroxide, sodium persulfate, and the like peroxides; water-soluble salts of the hypohalous acids in conjunction with an excess of base; and the alkali metal hypohalites in conjunction with an excess of an alkali metal hydroxide. Hydrogen peroxide and basic aqueous solutions of the alkali metal hypohalites are particularly suitable.

The ozonization of dissolved alpha-pinene, in accordance with the process of the present invention, can suitably be carried out in accordance with any of the con-

ventional procedures for the ozonization of a liquid. Where appreciable amounts of the pinene and the liquid ozonization medium are entrained by the ozone-containing gases, they are preferably liquefied and returned to the reactor.

The process of the present invention can suitably be conducted in a batchwise or a continuous manner. The preferred temperatures at which to conduct the ozonization in accordance with the process of this invention range from about −10° to +30° C. The preferred temperatures at which to decompose the ozonides so produced range from about 20° to 125° C.

The mixtures of pinene-derived acids provided by the present invention can be isolated by various separation procedures. For example, the unreacted pinene and/or the solvent can be extracted from the salts of the acids produced by decomposing the ozonides in a basic medium, and, after the salts are neutralized, the acids can be separated by extraction followed by fractional distillation. Where a hydroxy compound is used as the solvent, the acids can conveniently be esterified in situ and then the resulting esters can be separated by fractional distillation. The use of hexanol as the solvent and the separation of the acids by an esterification in situ followed by fractional distillation of the hexyl esters of the acids is a preferred method of producing and separating the pinene-derived acids in accordance with the present process. The esters so separated can, of course, be converted to the free acids by conventional ester cleavage reactions. And, of course, in the production of a mixture of esters provided by this invention, where the esters desired are those of an alcohol meeting the qualifications of the liquid ozonization medium, it is preferable to employ the alcohol as said medium and to form the esters in situ.

Unique and valuable mixtures of pinene-derived acids of two different groups composed of acids of closely related chemical and physical properties are provided by this invention.

The mixtures of the first of such groups consist of mixtures of pinene-derived acids composed substantially entirely of hydrocarbon dicarboxylic acids and predominating in pinic and norpinic acids, i. e. mixtures of acids all of which are pinene-derived acids which mixtures contain only trace amounts of acids having a structure other than that of the pinic and norpinic acids. One preferred group of such acids consists of a mixture of pinene-derived acids boiling between about 170° to 190° C. under a pressure supporting 0.5 mm. of mercury, having a refractive index (n_D^{20}) between about 1.475 to 1.485, and containing at least 80% pinic acids. Another preferred group of such acids consists of a mixture of pinene-derived acids that form a mixture of neutral hexyl esters boiling between about 140° to 170° C. under a pressure supporting 0.05 mm. of mercury, having a refractive index (n_D^{20}) between about 1.450 to 1.455, and containing at least 80% dihexyl pinates.

The mixtures of the second of such groups consist of mixtures of pinene-derived acids composed substantially entirely of keto-substituted monocarboxylic acids and predominating in pinonic and pinononic acids. One preferred group of such acids consists of a mixture of pinene-derived acids boiling between about 140° to 160° C. under a pressure supporting 0.5 mm. of mercury, having a refractive index (n_D^{20}) between about 1.465 to 1.475, and containing at least 80% pinonic acids. Another preferred group of such acids consists of a mixture of pinene-derived acids that form a mixture of neutral hexyl esters boiling between about 120° to 140° C. under a pressure supporting 0.05 mm. of mercury, having a refractive index (n_D^{20}) between about 1.455 to 1.460, and containing at least 80% hexyl pinonates.

The mixtures of keto-substituted monocarboxylic pinene-derived acids which are primarily composed of pinonic acid and pinononic acid provide (by virtue of their esterification reactions, and the properties imparted to the products of such reactions by the presence of the acyl radicals contained in them), mixtures which constitute valuable plasticizers when esterified with glycols such as ethylene and diethylene glycol, propylene glycol, butane-1,4-diol and the like.

The following examples are presented to illustrate in more detail certain features involved in the practice of this invention.

Example I

Use of a liquid ozonolysis medium which is also an ozonide-decomposing reagent.—Fifty ml. of alpha-pinene (0.31 moles) mixed with 150 ml. of acetic acid was ozonized at about 30° C. About 0.2 moles of ozonide was obtained. The acetic acid solution was diluted with an equal volume of water and heated at about 100° C. for 3 hours and the water and acetic acid were then removed in vacuo. 26.6 g. of semisolid product containing 0.1 equivalent of acid was obtained. Crystallization from ether and then from water gave 6.9 g. of acids, neutral equivalent=200, M. P. 89° to 91° C. From this mixture of acids pinonic acid, M. P. 103° C., neutral equivalent 185 was obtained by crystallization from benzene. A mixture of this acid with an authentic sample of pinonic acid (melting point 105° C.) melted at 104° to 105° C.

Example II

Use of an ozonolysis medium incompletely miscible with the amount of alpha-pinene used.—Fifty ml. (0.31 moles) of alpha-pinene was mixed with a mixture of 50 ml. of acetic acid and 50 ml. of water. Part of the alpha-pinene was not dissolved. This suspension was ozonized at 0° to 10° C. 0.2 moles of ozone was absorbed and the resultant solution contained 0.2 moles of ozonide. All the ozonide remained in solution. This acid solution of ozonide was refluxed for 1 hour, which treatment decomposed 80 percent of the ozonide. Removal of the solvents by distillation gave 36 g. of semisolid product containing 0.07 equivalent of acids.

Example III

Use of an ozonide-decomposition-controlling reagent during decomposition.—0.31 moles of alpha-pinene mixed with 100 ml. of 50 percent aqueous acetic acid was ozonized at room temperature (about 30° C.). 0.1 mole of ozone was absorbed and 0.1 mole of ozonide was present in the resulting solution. Substantial amounts of alpha-pinene were lost from the reactor by vaporization and entrainment but were recoverable with a suitable scrubbing system.

The resultant solution was divided in two equal parts. One part was refluxed for 1.5 hours at about 100° C. and the solvent was then removed by distillation at below 125° C. using vacuum as required. 8.5 g. of semisolid product containing 0.038 equivalent of acids was obtained. Analysis of the product by the method of Marvel and Rands (J. Am. Chem. Soc. 72, 2642 (1950) indicated that it contained 0.018 moles of pinonic acid.

The second part was adjusted to 3 percent hydrogen peroxide content by addition of 30 percent hydrogen peroxide and then treated in the same way as the first part. 9.4 g. of semisolid product containing 0.045 equivalent of acids of which 0.028 moles were pinonic acids was obtained.

Example IV

Use of an ozonide-decomposition-controlling reagent after decomposition.—0.31 moles of alpha-pinene mixed with 150 ml. of acetic acid was ozonized at 0° to 10° C. 0.21 moles of ozone was absorbed and an equal amount of ozonide was present in the resultant solution. Decomposition by refluxing at about 115° C. in the presence of 3 percent of hydrogen peroxide and removal of the solvent gave 44 g. of product containing 0.17 equivalent

of acids. This product was then refluxed for 2 hours with 50 ml. of 3 percent hydrogen peroxide and the solvent was again removed. 39 g. of product containing 0.17 equivalent of acids was obtained. Analysis of this product by the method of Marvel and Rands indicated the presence of 0.07 moles of pinonic acid and 0.035 moles of pinic acid.

Example V

Use of anozonolysis medium miscible with the ozonide-decomposing and ozonide-decomposition-controlling reagent.—0.31 moles of alpha-pinene was mixed with 150 ml. of methanol and ozonized at 0° to 10° C. The resultant solution contained 0.28 moles of ozonide. Dropwise addition of 600 ml. of a 6 N aqueous sodium hypochloride solution, containing 0.3 moles of excess sodium hydroxide, to the above solution, with vigorous stirring gave an exothermic reaction. Rate of addition was adjusted to maintain a temperature of 40° to 50° C. When all had been added (about 5 hours) the mixture was heated to 70° C. for 1 hour.

After evaporation of the methanol and extraction with chloroform to remove any neutrals, the basic aqueous phase was acidified with sulfuric acid and the acid products were isolated by extraction with chloroform. The chloroform solution was washed and dried and the solvent was then removed. About 20 g. of product, neutral equivalent 126, was obtained. Analysis by the method of Marvel and Rands indicates about 5 g. of pinonic acids and about 10 g. of hydrocarbon dicarboxylic acids including pinic acids.

Example VI

Analogous to Example V with different ozonide-decomposition-controlling reagent.—A solution of ozonide prepared in the manner described in Example V and containing 0.25 moles of ozonide was divided into three equal portions for decomposition.

0.08 moles of 5 N sodium hydroxide was added dropwise to one portion. The temperature rose to about 65° C. and was maintained by a suitable rate of addition of base. This addition required 40 minutes and the ozonide was substantially all decomposed. Neutrals were removed and the acids isolated as in Example V. 4.4 g. of acids, neutral equivalent=205 was obtained. The Marvel and Rands analysis indicated 2.7 g. of pinonic acids and 0.2 g. of pinic acids. The second portion was treated with 0.08 moles of base and 0.08 moles of hydrogen peroxide in the same manner as the first portion, and the product was recovered in the same way. 5.0 g. of acids, neutral equivalent=226 was obtained. The Marvel and Rands analysis indicated 2.9 g. of pinonic acids and 0.3 g. of pinic acids. The third portion was treated with 0.08 moles of hydrogen peroxide. There was no evidence of reaction so the solution was heated at 75° C. for 3 hours. At the end of this time the ozonide and peroxide content of the solution had not changed. Hence, 10 percent by volume of nitric acid (1:4) was added and the heating was continued for 4 hours. Over 95 percent of the original active oxygen content of the solution was decomposed. Evaporation under vacuum yielded a product containing 0.01 equivalent of acids.

Example VII

Ozonization and concurrent decomposition in an ozonolysis medium which is also a ozonide decomposing reagent.—0.5 moles of alpha-pinene and 0.5 moles of sodium hydroxide mixed with 140 ml. of methanol were ozonized at about 10° C. 0.48 moles of ozone was absorbed but no ozonide was present in the resulting solution and only 0.18 equivalent of free base remained. This solution was diluted with an equal volume of water and the neutrals were extracted with ether. The basic solution was then acidified and the acids were extracted with ether and isolated by removal of the solvent. 32 g. of product containing 0.08 equivalent of acid was obtained. Marvel and Rands analysis indicates 0.061 moles of pinonic acids and 0.005 moles of pinic acids.

Example VIII

Use of alcohol to be esterified as ozonization medium, esterification in situ and isolation of mixtures of esters.—50 ml. (0.31 moles) of alpha-pinene was mixed with 100 ml. of hexanol and ozonized at 0° to 10° C. using ozonized oxygen containing about 1 percent ozone. A clear solution containing 0.24 moles of ozonide was obtained. A total of 800 ml. of sodium hypochlorite solution (12%) was added slowly to the well-stirred ozonide solution, the rate of addition being adjusted to maintain a temperature of 40°±5° C. When the reaction was complete the mixture was acidified with sulfuric acid and the hexanol layer was separated. The pinene-derived acids remaining in the aqueous phase were recovered by ether extraction and added to the hexanol layer. About 0.3 equivalent of acids were obtained. Toluene (150 ml.) and sulfuric acid (3 ml. of 50%) were added and the mixture was refluxed for 2.5 hours to esterify the acids. Residual acid was removed by washing the solution with 40 ml. of 1 N base followed by two water washes. After removal of the toluene and hexanol about 60 g. of product was obtained. This was distilled at about 0.2 mm. to give the following cuts. Cut 1, 125° to 145° C. 12 g. $n_D^{20}=1.458$; cut 2, 19 g. 145° to 165° C. $n_D^{20}=1.453$. Cut 1 predominates in hexyl pinonates free from dicarboxylic esters and cut 2 predominates in dihexyl pinates free from mono carboxylic esters.

Example IX

Analogous to Example III but with a different ozonolysis medium.—100 g. of a solution of alpha-pinene ozonide in nitromethane containing 0.062 moles of the ozonide, prepared by ozonization of alpha-pinene mixed with three parts of nitromethane, substantially in the manner described in Example III was refluxed several hours to decompose the ozonide. Removal of the nitromethane in vacuo gave 16.3 g. of product containing 0.026 equivalent of acid. Of this, 0.021 equivalent was found to be pinonic acids by the Marvel and Rands analysis.

To a second 100 g. portion of the same ozonide solution (0.062 moles of ozonide) 11 g. of 30 percent hydrogen peroxide was added and the mixture was refluxed for several hours until both ozonide and hydrogen peroxide were decomposed. After removal of solvent in vacuo 18.7 g. of product containing 0.054 equivalent of acid was obtained. Of this 0.039 equivalent of pinonic acids and 0.007 equivalent of pinic acids were found by Marvel and Rands analysis.

Example X to XIII

Unique plasticizer properties of esters of the mixtures of acids provided by this invention.—A mixture of pinene-derived acids predominating in the pinic acids was esterified, by a conventional esterification procedure, with n-hexanol. The mixture of esters so produced was subjected to fractional distillation isolating a mixture of neutral n-hexyl esters boiling between about 140° and 150° C. under a pressure supporting 0.05 to 0.1 mm. of mercury, having a refractive index (n_D^{20}) between about 1.452 and 1.453, and containing at least 90% esterified pinic acid. Analogous mixtures of butyl cellosolve, n-amyl alcohol and n-octyl alcohol esters were prepared in an analogous manner.

A series of esters were incorporated to the extent of 35 or 40% in a commercially available vinyl resin (using Vinylite VYDR). The compositions so obtained were tested for tensile strength and elongation (using an IP-4 machine) at a loading rate of 200 pounds per minute at 70° F. with a relative humidity of 65±2%. The compositions were also subjected to a brittle test, basically that described as A. S. T. M. test D746-43T.

The values obtained are reported in the following table. Those obtained from the various mixtures of esters de-

scribed above are designated simply as the various alkyl "esters" numbers X to XIII. The values obtained from two commercially available di-octyl esters are reported for comparison.

	Tensile, p. s. i.	Modulus 100% elongation, p. s. i.	Ultimate elongation, percent	Brittle Point, ° C.
Compositions Containing 35% Ester:				
X. 2-butoxyethyl ester	2,794	1,252	316	−45
XI. Di-n-amyl ester	2,758	1,260	331	−44
XII. Di-n-hexyl ester	2,742	1,329	297	−49
XIII. Di-n-octyl ester	2,675	1,492	324	−54
Dioctyl phthalate	3,040	1,550	330	−33
Dioctyl sebacate	2,519	1,406	308	−58
Compositions Containing 40% ester:				
XIII. Di-n-octyl ester	2,285	1,178	354	−71
Dioctyl sebacate	2,176	874	350	−69

The above plasticized resin compositions were milled and molded at 300° F. and in each case the esters of the mixed pinene-derived acids produced a white or light cream colored sheet.

Those skilled in the art will recognize that the above tests demonstrate that unique and valuable properties are imparted to the above esters by the acyl radicals contained in the mixture of acids from which the esters were formed. In each of the properties tested the esters of the pinene-derived acids proved to be substantially equal to or better than the commonly employed commercially available plasticizers with which they were compared. The esters of the cyclic acids heretofore known (of individual acids or of mixtures of acids) have been characterized by their relative inefficiency as plasticizers. The discovery that these mixtures of esters of saturated cyclic acids plasticize a resin composition with approximately the same efficiency as do the corresponding esters of sebacic acid is a particularly unobvious valuable discovery in the field of resin chemistry.

Having thus described our invention we claim:

1. A process of ozonizing alpha-pinene to produce pinene-derived acids, comprising mixing alpha-pinene and methanol in proportion of one part alpha-pinene to about from 2 to 10 parts of methanol; contacting the mixture with an ozone containing gas; and subjecting the dissolved ozonides so produced to an acid producing decomposition by mixing with the solution containing them at least an equivalent amount of sodium hypochlorite and sufficient sodium hydroxide to make the mixture basic at about from 20° to 125° C.

2. A process of ozonizing alpha-pinene to produce pinene-derived acids, comprising mixing alpha-pinene and acetic acid in proportion of one part alpha-pinene to about from 2 to 10 parts of the acetic acid; contacting the mixture with an ozone containing gas; and subjecting the dissolved ozonides so produced to an acid producing decomposition by mixing with the solution containing them about from 0.1 to 2 parts of water at about from 20° to 125° C.

3. A process of ozonizing alpha-pinene to produce pinene-derived acids, comprising mixing alpha-pinene and an unreactive liquid ozonolysis medium selected from the group consisting of alkanols, alkanoic acid, and nitroparaffins which are appreciably miscible with both alpha-pinene and the ozonide of alpha-pinene; contacting the mixture with an ozone-containing gas; and subjecting the dissolved ozonides so produced to an acid producing decomposition by mixing with the solution containing them about from 0.1 to 2 parts of water and about from 0.01 to 0.03 part of hydrogen peroxide at about from 20° to 125° C.

4. The process of claim 3 in which the liquid ozonolysis medium is acetic acid and in which the alpha-pinene and acetic acid are in proportion of one part alpha-pinene to about from 2 to 10 parts of acetic acid.

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