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LOWER ALKANOIC ESTERS OF CYCLIC HEMI-ACETALS AND THEIR PREPARATION

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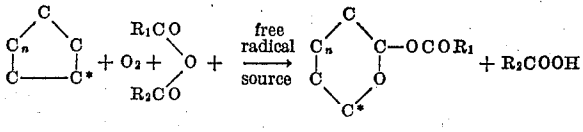
This invention relates to a process of producing lower-alkanoic esters of cyclic hemi-acetals.

An object of the invention is to provide a simple, economical, one-step process of producing said esters, some of which are entireley new chemicals that cannot be otherwise produced.

According to the invention said esters are produced by treating selected cyclic hydrocarbons with gaseous oxygen, in a solvent medium which is an anhydride of a lower alkanoic acid and in the presence of a source of free radicals.

Regardless of the mechanism involved, the net results of the reaction are (1) to enlarge a non-benzenoid five-carbon or six-carbon ring of the hydrocarbon by the insertion of an inner-ether oxygen atom at a particular point in the ring; and (2) to replace a hydrogen atom of a methylene group alpha to the ether oxygen, by an acyloxy group, thereby forming a carboxylic ester of a cyclic hemi-acetal. This reaction is shown schematically as follows:

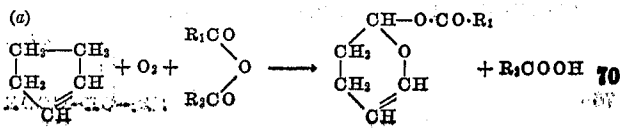


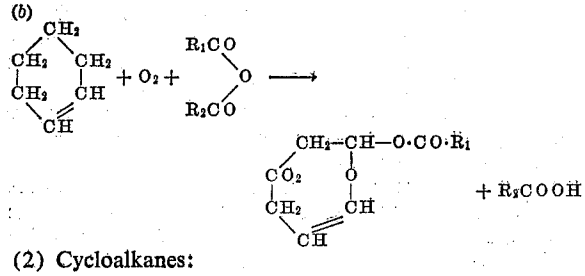
in which R_1 and R_2 are the same or different alkyl groups, each of which contains no more than three carbon atoms; the letter n is a positive integer not greater than two; and the starred carbon atom carries not more than one hydrogen atom; i.e., this carbon atom is ternary or quaternary. This latter limitation permits ring enlargement without degradative oxidation; such a carbon atom is found in cycloalkenes and in those hydrocarbons which contain a ring-carbon atom attached to at least three other carbon atoms. When the hydrocarbon contains both a non-olefinic ring carbon atom which is attached to at least three other carbon atoms, and an olefinic group >C=C< in such a position in the ring that the olefinic group and the said carbon atom do not activate the hydrocarbon toward attack by oxygen at the same point in the ring, the oxygen attacks the ring preferentially at a point adjacent to the olefinic group. The ring is non-aromatic, but the starred carbon and the one next to it may also form part of a second ring which can be benzenoid.

The hydrocarbons used belong to three classes, viz: (1) cycloalkenes, (2) alkylcycloalkanes, and (3) benzocycloalkanes.

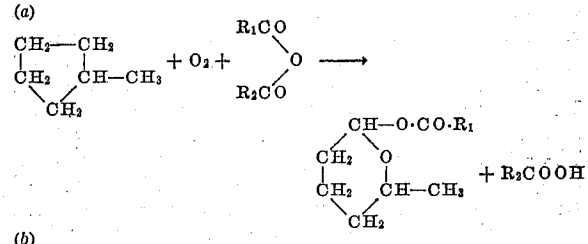
The reaction of this invention is illustrated further by the following typical equations:

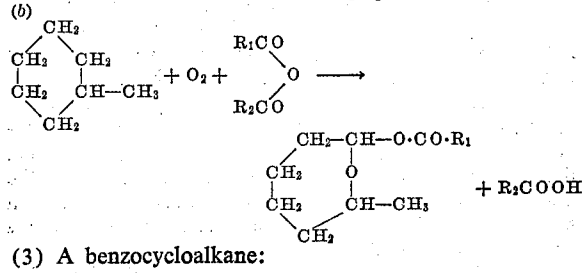
(1) Cycloalkenes:



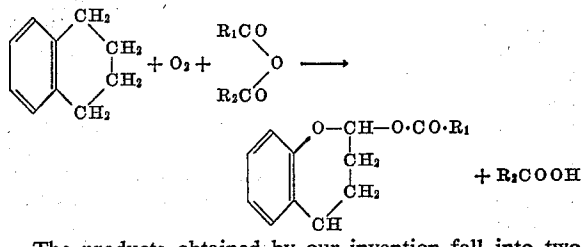


(2) Cycloalkanes:





(3) A benzocycloalkane:



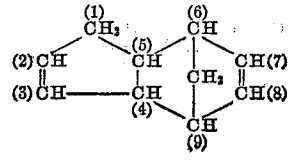
The products obtained by our invention fall into two distinct classes depending on the hydrocarbons used in the reaction.

Of the hydrocarbons which we employ, only the cyclic olefinic hydrocarbons are converted by our process into compounds, which, as we shall show hereinafter, can be considered to be the stable equivalents of potentially valuable but usually unstable dialdehydes or keto-aldehydes. The hydrocarbons which belong to the other two groups—those which lack an olefinic group in a five- or six-membered ring—do not have this desirable property. Therefore, that embodiment of our invention which employs cyclic olefinic hydrocarbons is considered the most valuable.

To react in the sense of our invention, the hydrocarbons must contain a group of aliphatic character attached to a ternary or quaternary carbon atom.

Typical cycloalkenes which are operable in our invention are cyclopentene, cyclohexene, 3-methylcyclopentene, 3-methylcyclohexene, the dimethylcyclohexenes, and dicyclopentadiene.

The polycyclic compound dicyclopentadiene is both a cyclopentene (carbons 1, 2, 3, 4 and 5) and a cyclohexene (carbons 4, 5, 6, 7, 8 and 9) having a 6,9-bridge.



Typical cycloalkanes having a tertiary carbon atom, operable in our invention, are methylcyclopentane, methylcyclohexane, the dimethylcyclopentanes, and the dimethylcyclohexanes.

Typical polycyclic aromatic hydrocarbons which are operable in our invention are indene, tetralin and 9,10-dihydroanthracene. The aromatic hydrocarbon must have a non-benzenoid ring fused to a benzenoid ring by two carbon atoms which are common to both rings, to serve as a focus for attack by oxygen in our process.

The esters made by our invention are useful as solvents for many organic materials. In particular, the esters dissolve and plasticize many plastic materials such as polyvinyl chloride and heteropolymers of vinyl chloride with vinyl acetate or vinylidene chloride. Thus, the esters can be used to make lacquers or pastes from vinyl chloride polymers. The lacquers can be brushed or sprayed onto textile fabrics and paper to form useful products suitable for upholstery, luggage, raincoats, etc. The pastes can be applied to fabrics and paper by means of a calender or doctor knife to form similar products. The esters which have fairly low boiling points are especially suitable as solvents because they can be evaporated from the vinyl chloride polymer film or coating. The esters which have higher boiling points are particularly useful as plasticizers, because it is preferable that they should not evaporate from the said polymer—especially when the final products must retain flexibility.

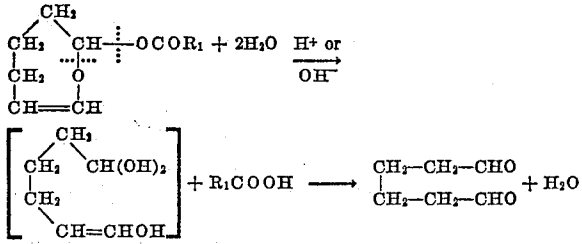
In general, the mixtures of ester and polymer should be warmed slightly, e.g., to 60–80° C., to hasten solution of the polymer. This heating also is necessary when the ester melts above room temperature. (Most of the esters made by this invention are liquids which have a pleasant, sometimes fruity, odor. The remaining esters are low-melting solids.)

All of the esters made by the reaction of this invention can be hydrolyzed, by either acid (H^+) or alkali (OH^-) to form difunctional compounds. However, the various esters are distinguishable among themselves both from the standpoint of their behavior on hydrolysis and from the standpoint of the uses of the hydrolyzed derivatives.

The esters made from cyclic olefinic hydrocarbons are hydrolyzed to compounds which contain two carbonyl groups (two aldehyde groups, two ketone groups, or an aldehyde group and a ketone group). On the other hand, the esters made from cyclic non-olefinic hydrocarbons are hydrolyzed to compounds which contain one aldehyde or ketone group and one alcohol or phenol group. This difference is illustrated by the following equations which show correctly the products of the hydrolysis of specific esters, but which do not necessarily show the correct mechanism of reaction:

Hydrolysis of esters made from cycloolefins—

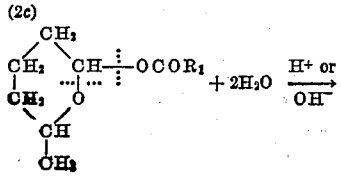
(1c)

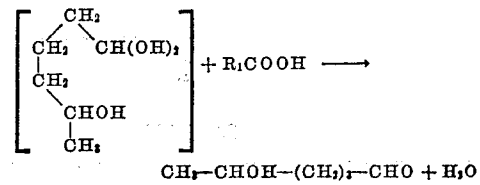


Adipaldehyde

Hydrolysis of esters made from cycloparaffins—

(2c)

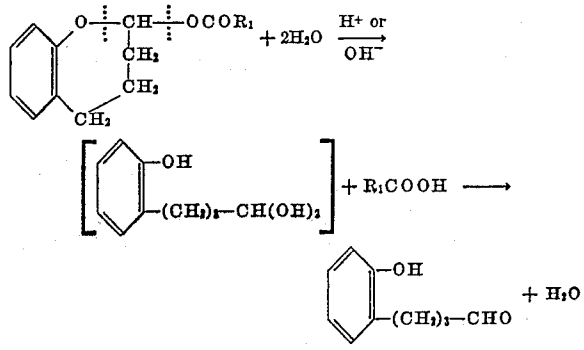




5-hydroxycaproaldehyde

Hydrolysis of esters made from aromatic hydrocarbons—

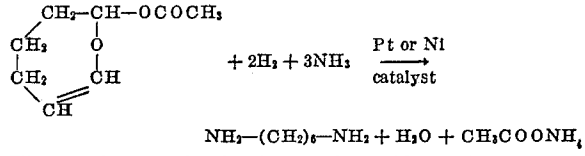
(3c)



4-(o-hydroxyphenyl)-butyraldehyde

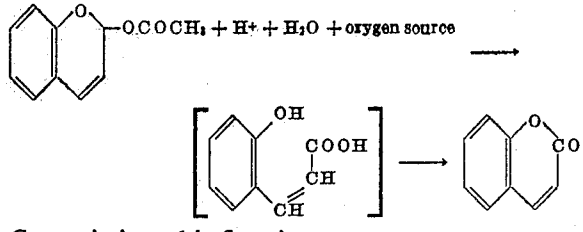
In actual practice we do not isolate the primary products of hydrolysis of the esters, especially when such products are dialdehydes and the like. Instead we react the esters directly with any desired reagents in the presence or absence of water according to the individual reaction desired. Three such reactions are shown .

2-oxa-3-cycloheptenyl acetate is converted to hexamethylene diamine by reductive amination under anhydrous conditions, as follows:



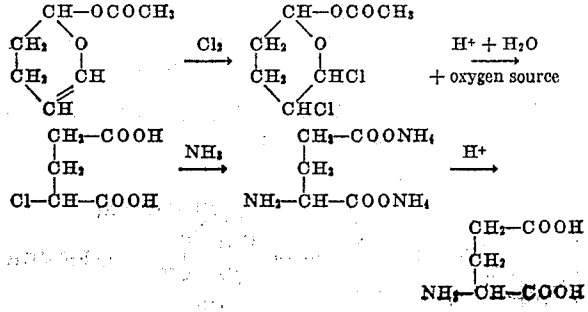
Hexamethylene diamine is used in making nylon.

Indene is converted to 2-(1-oxa-1,2-dihydronaphthyl) acetate by the method of our invention. The ester is hydrloyzed in aqueous acid under conventional oxidizing conditions to form beta-(o-hydroxyphenyl)-acrylic acid, which spontaneously esterifies intramolecularly to form coumarin, as follows:



Coumarin is used in flavorings.

2-oxa-3-cyclohexenyl acetate is converted to glutamic acid by the following reactions:



Monosodium glutamate, which is easily made from glutamic acid and one molar equivalent of sodium hydroxide, is used to enhance the flavor of foods.

The anhydride used in our process is one formed from a lower alkanoic acid; e.g., an acid preferably containing from two to four carbon atoms. Such anhydrides are acetic anhydride, propionic anhydride, butyric anhydride, and isobutyric anhydride. Mixed anhydrides, e.g., acetic butyric anhydride, also can be used. For economic reasons we prefer to use acetic anhydride. The anhydride acts not only as a solvent and as one of the reagents but also, in some further way not fully understood, it accelerates the reaction. In other words, the anhydride is necessary in the operation of our invention. The fact that the solvent medium in the present process in an anhydride necessarily and inherently means that the medium is anhydrous, since any water present would of course be consumed by the anhydride. On the other hand, if an excess of water were present then the medium obviously would not be an anhydride, and the purposes of the invention of course would not be served. It will therefore be clear that the present disclosure of an anhydride as the solvent medium necessarily implies an anhydrous reaction medium.

The amount of anhydride per mole of hydrocarbon can range between about 0.5 mol and about 8 mols. The hydrocarbon and anhydride react in equimolar amounts, but, as we point out hereinafter, it is desirable to interrupt the reaction long before all of the hydrocarbon has reacted. Our preferred range is from about one mol to about 4 mols of anhydride per mol of hydrocarbon.

The catalyst used in our reaction can be any agent customarily used to generate free radicals. Such agents are the peroxidic catalysts, e.g., the acyl peroxides, the alkyl and cycloalkyl peroxides, the alkyl and cycloalkyl hydroperoxides, and the peroxy acids and salts, e.g., the persulfates; the decomposable azo compounds, e.g., N,N'-azobis-(alpha-isobutyronitrile) (also called "Porofor N"); and ultraviolet light. Such agents are well known, especially as initiators of polymerization reactions. The catalyst, except, of course, ultraviolet light, can be added to the reacting hydrocarbon entirely at the beginning of the reaction, or it can be added gradually throughout the reaction. When the catalyst is ultraviolet light, irradiation can be intermittent, or continuous. Sufficient ultraviolet light goes through Pyrex glass to effect catalysis. Quartz glass also can be used.

The oxygen can be used either in pure condition or mixed with inert gaseous material. The most common mixture is air.

The process is operable at temperatures between about 20° C. and about 150° C. Of course, the temperature and the catalyst are interrelated. The temperature must be high enough so that free radicals are formed at a reasonably fast rate, and low enough so that the catalyst does not decompose too fast and so that the desired products are stable. Temperatures above 150° C. are unsuitable because of the latter consideration. Temperatures below 20° C. are unsuitable because the reaction is too slow to be practical. Our preferred temperature range is from about 50° C. to about 100° C. We have found that, within this preferred range, typical catalysts which form free radicals at a suitable rate are Porofor N, ultraviolet light and benzoyl peroxide. Catalysts such as tertiarybutyl peroxide which form free radicals at an appreciable rate only at temperatures above 100° C., also are operable in our invention.

The new reaction can be carried out either batchwise or continuously. In either case it is advisable to separate the desired ester from unreacted materials, e.g., by fractional distillation, as soon as conversion of the hydrocarbon to the desired ester reaches about 10%, because the ester is slowly converted to higher-boiling materials in the reaction medium. If the reaction is continued too long the ester is destroyed substantially as fast as it is formed, and the concentration of the ester never rises much above a value equal to 15% mol-percent of the original hydrocarbon. Therefore, undesirable destruction of the desired ester, with consequent loss of yield and waste of material, is avoided, by removing the ester substantially as soon as the conversion reaches a value equal to about 10%–15%, as will be made apparent in more detail in the working examples below.

The following examples illustrate our invention; all parts and percentages are by weight:

Example 1

A mixture of 820 parts of cyclohexene, 1617 parts of acetic anhydride and 3 parts of Porofor N was held at 85–90° C. for 48 hours. Throughout this time oxygen was bubbled through the solution. The exit gas passed through a reflux condenser and a Dry-Ice trap. At the end of this period the solution was fractionally distilled under reduced pressure to remove unreacted cyclohexene and acetic anhydride, as well as the acetic acid which was formed in the reaction. The cyclohexene and acetic acid distilled as an azeotrope, which was separated into its two components with potassium carbonate. The recovery of cyclohexene was 342 parts.

The higher-boiling material was fractionally distilled through a packed column with partial reflux. The desired product, 2-oxa-3-cycloheptenyl acetate, boiled at 52° C. at 3.5 mm. Hg. The yield was 145.2 parts, or 16.0% of theory. It is a water-clear mobile liquid with a fruity, ester-like odor.

n_D^{20} 1.4580, d_{20}^{20} 1.0756

The ester is stable in the presence or absence of dry air.

Analysis.—Calcd. for $C_8H_{12}O_3$: carbon 61.52%, hydrogen 7.69%. Found: carbon 61.61%, hydrogen 7.63%.

The molar refraction, when calculated from density and refractive index, is 39.6; when calculated by summation of those of individual groups (as shown, e.g., by Lange, Handbook of Chemistry, 6th edition, page 1025), it is 39.65.

This ester is a good solvent for polyvinyl chloride (e.g., Marvinol VR–10, Marvinol VR–20 and Marvinol VR–30), for vinyl chloride:vinyl acetate copolymers (eg., Vinylite VYNW 96:4), and for vinyl chloride:vinylidene chloride copolymers (e.g., the Sarans).

This new compound was reduced with lithium aluminum hydride, yielding 1,6-hexanediol.

This acetate does not liberate iodine from a solution of potassium iodide in acetic acid, thus showing that it cannot be the isomeric compound cyclohexenyl peroxyacetate.

Our new acetate decolorizes bromine (in carbon tetrachloride) and dilute aqueous potassium permanganate instantly. Glutaric acid was isolated from the permanganate reaction. These facts show that the olefinic group of the cyclohexene is present in the ester, and that this group is adjacent to the ring oxygen; i.e., that there are three contiguous methylene groups separated from the ring oxygen by at least one carbon atom. Infrared analysis confirms the presence of both the C=C group and the ester group in our new acetate.

In the presence of aqueous acid or aqueous alkali this new ester undergoes reactions that are characteristic of adipaldehyde. The following experiments show how useful derivatives of adipaldehyde can be made directly from this cyclic acetate.

A. A warm solution of 2,4-dinitrophenylhydrazine in 95% ethanol, to which a few drops of concentrated hydrochloric acid had been added, was mixed with a warm solution of our new acetate in 95% ethanol. A tan precipitate of the bis-(2,4-dinitrophenylhydrazone) of adipaldehyde formed within a few minutes. It melted at 229–231° C. with decomposition. It is almost insolu-

ble in ethanol, ethyl acetate or chloroform. After recrystallization from nitrobenzene it melted at 233–234° C. with decomposition.

Analysis.—Calcd. for $C_{18}H_{18}N_8O_8$: C, 45.55%, H, 3.80%, N, 23.63%. Found: C, 45.87%, H, 4.00%, N, 23.23%.

An authentic sample of adipaldehyde made, just before use, by the method given in Beilstein 1, 787, was treated with 2,4-dinitrophenylhydrazine in like manner. The dihydrazone was identical with that formed from our new ester, as shown by a mixed melting point determination.

B. An aqueous solution of hydroxylamine hydrochloride was made alkaline with sodium hydroxide. Then a small amount of our new acetate was added. Ethanol was added gradually until the solution became homogeneous. The solution was heated on the steam bath for ten minutes, and then was cooled. The dioxime of adipaldehyde crystallized as a white powder. After recrystallization from ethanol it melted at 178–179° C. The melting point could not be raised further. (Wohl and Schweitzer—Ber. 39, 894—report the melting point as 185–186° C.)

Analysis.—Calcd. for $C_6H_{12}N_2O_2$: C, 50.00%, H, 8.25%, N, 19.45%. Found: C, 50.12%, H, 8.08%, N, 19.58%.

The dioxime also was made from freshly prepared adipaldehyde. Both its melting point, and the mixed melting point with the dioxime prepared from our new acetate, were 178–179° C.

Experiments A and B of Example 1 show that 2-oxa-3-cycloheptenyl acetate can be considered to be a stable, easily prepared equivalent of the unstable, difficultly prepared adipaldehyde.

Examples 2–5

These examples show the effect of varying the time of reaction and the amount of catalyst on the yield of the ester. Oxygen was passed through each solution at 75–80° C. under the conditions shown. When the oxidation was stopped the solution was fractionally distilled in vacuo.

	Ex. 2	Ex. 3	Ex. 4	Ex. 5
Materials Charged:				
Cyclohexene	1,350	1,350	1,350	1,350
Acetic anhydride	1,840	1,840	1,840	1,840
Porofor N	[a] 1	[a] 4	[b] 4	[b] 8
Reaction time (hours)	6	6	24	48
Distilled Fractions (in ascending order of boiling point):				
Cyclohexene	1,010	997	796	487
Acetic acid	120	105	268	659
Acetid anhydride	1,463	1,647	1,417	1,005
Intermediates	139	186	173	283
2-Oxa-3-cycloheptenyl acetate	150	176	293	301
Intermediates		26	19	
Undistilled residue	70	126	256	755
Percentage conversion to 2-oxa-3-cycloheptenyl acetate	5.8	6.8	11.4	11.7
Percentage yield based on cyclohexene used up	23.2	26.0	27.8	18.3

[a] Added at beginning of reaction.
[b] One part added at each six-hour interval.

These examples show that the optimum reaction time of reaction, under the particular conditions shown, was about 24 hours. A time of six hours was too short to obtain the maximum amount of the desired ester, regardless of the amount of catalyst used. A time of 48 hours not only did not increase the amount of the ester but also was wasteful of reagent in that higher-boiling material was formed—presumably by decomposition or polymerization of the ester—at the expense of cyclohexene.

Examples 6–8

Each of three mixtures of 246 parts of cyclohexene and 459 parts of acetic anhydride was put into an ultraviolet irradiation flask of the type described by Kharasch and Friedlander—J. Org. Chem. 14, 239 (1949). Oxygen was bubbled through the solutions, while they were being irradiated, for 24 hours at the respective temperatures designated below. The exit gases were passed through a Dry-Ice trap to condense organic material swept out of the flask by the oxygen. Then each solution, including the material in the trap, was fractionally distilled in vacuo. The results are shown as follows:

	Ex. 6	Ex. 7	Ex. 8
Temperature of oxidation (°C.)	25–29	50–55	78–82
Total weight of oxidized solution	700	705	727
Yield of 2-oxa-3-cycloheptenyl acetate (parts)	12	32	37
Higher-boiling residue (parts)	8	25	68

The residues from these solutions were much lighter in color than those (Examples 1–5) wherein the catalyst was Porofor N.

Examples 6–8 show that ultraviolet light is a suitable catalyst in the operation of our invention, and that the temperature of the reaction can be varied widely. They also show that the time and temperature of the reaction are correlated. Example 7 represents the optimum conditions in this series of three. The experiment of Example 6 was run too short a time for optimum conversion at the low temperature used, while that of Example 8 was run too long a time, as shown by the changes in the yields of the desired ester and the higher boiling residue.

Example 9

A mixture of 192 parts of 3-methylcyclohexene and 408 parts of acetic anhydride was irradiated with ultraviolet light, in the apparatus described in Example 6, for 40 hours at 55–65° C. while oxygen was bubbled through it continuously. The total weight of the treated solution, including that in the trap, was 660 parts. The solution was fractionally distilled in vacuo. The desired product boiled at 61–62° C. at 2 mm.; n_D^{20} 1.4583. It is 2-oxa-1-methyl-3-cycloheptenyl acetate and/or 2-oxa-5-methyl-3-cycloheptenyl acetate. We believe that the product is a mixture of the two isomers, because ring enlargement of 3-methylcyclohexene can take place on either side of the olefinic group. The yield was about 15 parts. The undistillable residue weighed 185 parts. It was evident from these yields and from the rate of oxygen absorption that the reaction is much faster than that of Examples 6–8, and that the reaction was run much longer than optimum.

Analysis.—Calcd. for $C_9H_{14}O_3$: C, 63.53%, H, 8.24%. Found: C, 63.72%, H, 7.96%.

This ester dissolves polyvinyl chloride, and copolymers of vinyl chloride with vinyl acetate and with vinylidene chloride.

Example 10

A mixture of 197 parts of cyclohexene and 468 parts of propionic anhydride was treated with oxygen, in the apparatus described in Example 6, for 18.5 hours at 50° C. and then for 5.5 hours at 60° C. The mixture was then fractionally distilled in vacuo. The desired product, 2-oxa-3-cycloheptenyl propionate, boiled at 44–48° C. at 0.4 mm.; n_D^{20} 1.4586; yield 28.5 parts.

Analysis.—Calcd. for $C_9H_{14}O_3$: C, 63.53%, H, 8.24%. Found: C, 63.64%, H, 8.34%.

This ester dissolves polyvinyl chloride, and copolymers of vinyl chloride with vinyl acetate and with vinylidene chloride.

The 2,4-dinitrophenylhydrazone and the oxime formed from this ester are identical to those formed from the acetate of Example 1. Thus, both esters are stable equivalents of adipaldehyde in the preparation of derivatives.

Examples 1–10 illustrate the use of the method of our invention in oxidizing cyclohexenes. Examples 11 and 12 show the treatment of cyclopentenes by our method.

Example 11

A mixture of 200 parts of cyclopentene and 459 parts of acetic anhydride was treated with oxygen, as shown in Example 6, for 24 hours at 50° C. The mixture was then fractionally distilled in vacuo. The product 2-oxa-3-cyclohexenyl acetate, boiled at 47–49° C. at 3 mm.; n_D^{20} 1.4532; d_4^{25} 1.107; yield 16.5 parts.

Analysis.—Calcd. for $C_7H_{10}O_3$: C, 59.14%, H, 7.04%. Found: C, 59.34%; H, 6.90%.

This ester dissolves polyvinyl chloride, and copolymers of vinyl chloride with vinyl acetate and with vinylidene chloride.

This ester was converted to the known 2,4-dinitrophenylhydrazone of glutaraldehyde, M.P. 189–190° C.

Example 12

A mixture of 322 parts of freshly distilled dicyclopentadiene and 373 parts of acetic anhydride was treated with oxygen, as in Example 6, for 3.5 hours at 50–54° C. The mixture then was fractionated in vacuo. The product, an acetic ester whose structure has not been determined, boiled at 49–50° C. at 0.15 mm.; n_D^{20} 1.5238. It formed a red 2,4-dinitrophenylhydrazone which melted at 182–183° C. after recrystallization from 95% ethanol.

Example 13 shows the treatment of a cyclic saturated hydrocarbon by the method of our invention.

Example 13

A mixture of 245 parts of freshly distilled methylcyclohexane and 382 parts of acetic anhydride was oxidized, as in Example 6, for 26.5 hours at 70° C. and then for 24 hours at 98–99° C. After this treatment the mixture, which remained homogeneous at room temperature, was fractionally distilled in vacuo. The product, 2-oxa-1-methylcycloheptyl acetate, boiled at 50–52° C. at 0.002 mm.; n_D^{20} 1.4389; d_4^{24} 1.012; yield 10 parts.

Analysis.—Calcd. for $C_9H_{16}O_3$: C, 62.76%, H, 9.35%. Found: C, 62.26%, H, 9.17%.

This ester dissolves polyvinyl chloride, and copolymers of vinyl chloride with vinyl acetate and with vinylidene chloride.

Example 14 shows the treatment of an aromatic hydrocarbon having a non-aromatic ring by our method.

Example 14

A mixture of 331 parts of redistilled tetralin and 383 parts of acetic anhydride was treated with oxygen in the apparatus described in Example 6, for 21.5 hours at 50–54° C. and then for 17.5 hours at 70–73° C. The mixture was fractionally distilled in vacuo. The desired product, bicyclo - [5,4,0] - 2 - oxa - 8,10,1 - hendecatrien - 3 - yl acetate, was thus separated as a crude yellow oily solid. The yield was 81 parts. After recrystallization from 95% ethanol it appeared as snow white platelets which melted at 60–61° C.

Analysis.—Calcd. for $C_{12}H_{14}O_3$: C, 69.90%, H, 6.85%. Found: C, 69.93%, H, 7.17%.

This ester dissolves and plasticizes polyvinyl chloride, and copolymers of vinyl chloride with vinyl acetate and with vinylidene chloride.

Having thus described our invention, what we claim and desire to protect by Letters Patent is:

1. A method of making alkanoic esters of cyclic hemiacetals which comprises intimately contacting gaseous oxygen with a cyclic hydrocarbon mixed with an anhydride of a lower alkanoic acid in the presence of a free radical producing initiator, at a temperature of from about 20° C. to about 150° C., the proportion of anhydride ranging from about 0.5 to 8 mols per mol of hydrocarbon, the hydrocarbon containing from five to six carbon atoms in the ring and being selected from the class consisting of cycloalkanes having at least one ring carbon atom attached to at least three other carbon atoms, cycloalkenes, and benzocycloalkanes having an alicyclic ring fused to a benzene ring.

2. A method of making alkanoic esters of cyclic hemi-acetals which comprises intimately contacting gaseous oxygen with a cyclic hydrocarbon mixed with an anhydride of a lower alkanoic acid in the presence of a free radical producing initiator from the class consisting of organic peroxide compounds, azo compounds, and ultraviolet rays, at a temperature of from about 20° C. to about 150° C., the proportion of anhydride ranging from about 0.5 to 8 mols per mol of hydrocarbon, the hydrocarbon containing from five to six carbon atoms in the ring and being selected from the class consisting of cycloalkanes having at least one ring carbon atom attached to at least three other carbon atoms, cycloalkenes, and benzocycloalkanes having an alicyclic ring fused to a benzene ring.

3. A method as set forth in claim 1 in which the hydrocarbon is a cycloalkane.

4. A method as set forth in claim 3 in which the hydrocarbon is methylcyclohexane.

5. A method as set forth in claim 1 in which the hydrocarbon is a cycloalkene.

6. A method as set forth in claim 5 in which the hydrocarbon is cyclohexene.

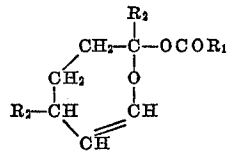
7. A method as set forth in claim 5 in which the hydrocarbon is 3-methylcyclohexene.

8. A method as set forth in claim 1 in which the hydrocarbon is dicyclopentadiene.

9. A method as set forth in claim 1 in which the hydrocarbon is a benzocycloalkane.

10. A method as set forth in claim 9 in which the hydrocarbon is tetralin.

11. The esters which have the structure

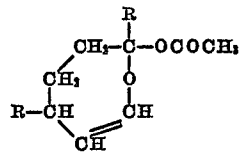


wherein R_1 is an alkyl group containing no more than three carbon atoms, and R_2 is chosen from the class consisting of hydrogen and methyl, and wherein at least one R_2 is hydrogen.

12. 2-oxa-3-cycloheptenyl acetate.

13. 2-oxa-3-cycloheptenyl propionate.

14. A methyl-2-oxa-3-cycloheptenyl acetate which has the structure



wherein one of the radicals R is hydrogen and the other is methyl.

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