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PREPARATION OF HYDROCARBON SUBSTITUTED SUCCINIC ACID ANHYDRIDES

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This invention relates to a novel process for preparing valuable hydrocarbon substituted succinic acid anhydrides. More particularly, the invention is concerned with an improved new process for preparing superior alkyl and cycloalkyl succinic anhydrides in enhanced yields from alkanes or cycloalkanes and maleic anhydride.

Hydrocarbon substituted succinic anhydrides are valuable for a variety of uses including their application as rust inhibitors and capillary agents. They are also useful intermediates in the production of esters which are valuable as plasticizers and superior synthetic oils for lubricating purposes.

Certain hydrocarbon substituted succinic anhydrides, namely, the alkenyl succinic anhydrides, may be prepared by the condensation of monoolefins and maleic anhydride. Although these alkenyl succinic anhydrides and their ester derivatives have been employed in some of the above-described applications, they are generally unsatisfactory due to their susceptibility to oxidation which results in either destruction and loss of the compound or its deterioration into undesirable products such as tars and coke at high temperatures. For these reasons, the saturated hydrocarbon substituted succinic acid anhydrides, more specifically, the alkyl succinic anhydrides and their ester derivatives, are clearly preferred since they are much more resistant to oxidation.

Up to the present, however, the production of saturated hydrocarbon substituted succinic anhydrides, such as the alkyl succinic anhydrides, has been subject to several serious disadvantages. The processes in general have been complicated and expensive to operate and the yields have not been satisfactory. One particular disadvantage characteristic of the processes proposed heretofore has been in the two-step procedure of first condensing a monoolefin with maleic anhydride and then subjecting the unsaturated alkenyl succinic anhydride product thus obtained to carefully controlled, mild hydrogenation just sufficient to saturate the olefinically bonded carbon atoms. A further disadvantage in the previously suggested processes has been the need for monoolefinic hydrocarbons which are in general demand and therefore sometimes difficult as well as expensive to obtain.

It has now been found that superior alkyl succinic acid anhydrides and cycloalkyl succinic acid anhydrides can be conveniently prepared in enhanced yields by an improved new process which comprises reacting a member of the group consisting of alkanes and cycloalkanes of from 3 to 40 carbon atoms with maleic anhydride in the presence of a peroxide free radical initiator catalyst.

The process, according to the invention, is straightforward and economical in operation. Excellent yields of the desirable oxidation resistant alkyl succinic anhydrides are obtained. A particular advantage of the process lies in the fact that the alkyl succinic anhydrides are produced in a single-step reaction, thus avoiding the complications and expense of extra equipment and loss in yields due to extra handling encountered in previously proposed two-step procedures. A further, more distinct advantage of the process according to the invention, however, lies in the fact that it employs the more readily available alkanes and cycloalkanes rather than monoolefinic hydrocarbons.

The alkanes and cycloalkanes employed in the process according to the invention as previously mentioned con-

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tain from 3 to 40 carbon atoms. Suitable alkanes and cycloalkanes, which may also be referred to as paraffins and cycloparaffins, include propane, butane, 2,3-dimethyl butane, cyclopentane, methylcyclopentane, cyclohexane, methylcyclohexane, nonane, dodecane, hexadecane or cetane, eicosane, propylcyclohexane, triacontane, and the like. Paraffin waxes are also suitable. For present purposes, branched chain alkanes and cycloalkanes, particularly those containing from 6 to 32 carbon atoms, are preferred since they provide superior yields of the desired alkyl and cycloalkyl succinic anhydrides. Illustrative examples of such preferred branched chain alkanes and cycloalkanes include 2,3-dimethylbutane, methylcyclopentane, methylcyclohexane, and ethylated waxes obtained by reacting paraffin waxes with ethylene in the presence of an alkyl halide catalyst as described in U.S. Patent No. 2,741,649, issued April 10, 1956, to Abbott and Brooke.

As mentioned, maleic anhydride is employed in the process of the invention. Examples of other acids or acid anhydrides which may be reacted with alkanes or cycloalkanes in accordance with the invention include citraconic acid, ethylmaleic acid, glutaconic acid, itaconic acid, methylitaconic acid, etc.

According to the process of the invention the alkanes or cycloalkanes are reacted with maleic anhydride in the presence of a peroxide free radical initiator catalyst. Heating may be employed to promote the reaction. However, an advantage of the present process lies in the fact that unusually high temperatures are unnecessary. Thus, loss in yields due to thermal splitting of the reactants and products is avoided. For present purposes reaction temperatures of from about 220° F. (104° C.) to about 400° F. (204° C.) are preferred. The best yields of alkyl and cycloalkyl succinic anhydrides are apparently obtained with reaction temperatures in the range from about 280° (138° C.) to about 350° F. (177° C.) and these temperatures are still more preferred accordingly.

The alkanes or cycloalkanes may be reacted with the maleic anhydride at any suitable pressure. Pressures sufficient to maintain the reactants in a liquid state can be used to facilitate handling and avoid loss of materials. For present purposes autogenous pressures developed in a closed system by the reactions are found to be very satisfactory.

The reaction according to the process of the invention may be carried out over any period of time necessary to desired completion. Ordinarily, reaction times of from about 10 to about 20 hours are sufficient for batch-type operations. Either shorter or longer reaction times may be employed to complete the reaction to the desired degree depending on the reactants and reaction conditions.

A peroxide free radical initiator catalyst is employed in the process of the invention as previously mentioned. Such catalysts include benzoyl peroxide, acetyl peroxide, tertiarybutyl hydroperoxide, ditertiarybutyl peroxide, dibenzoyl peroxide or ditertiaryamyl peroxide. Organic peroxide free radical initiator catalysts of these types are particularly suitable. However, for present purposes, ditertiarybutyl peroxide is the preferred free radical initiator catalyst since it provides outstanding yields of alkyl and cycloalkyl succinic anhydrides.

The alkanes or cycloalkanes are reacted with the maleic anhydride in equimolar proportions. Excess alkane or cycloalkane is ordinarily employed up to tenfold molar excess in order to insure as complete reaction as possible. Unreacted alkane or cycloalkane is readily separated from the reaction mixture and may be recovered and recycled to the process.

The following examples are offered in further illustration of the invention. Unless otherwise specified, the proportions are given on a weight basis.

EXAMPLE I

In this example cetane was reacted with maleic anhydride to produce cetyl succinic acid anhydride. The following materials were charged to a pressure bomb and maintained at a temperature of 284° F. for 12 hours:

Cetane, g----- 1000 (3.5 mol).
Maleic anhydride, g----- 196 (2.0 mol).
Di-tert-butyl-peroxide, g----- 50.

After the reaction period the bomb was emptied and found to contain 250 g. of solid product and 952 g. of liquid. The liquid was distilled, yielding 872 g. of unreacted cetane and 80 g. of bottoms product which was the desired material. This material was readily soluble in benzene and on analysis gave the following results:

	Found	Theory For Cetyl Succinic Anhydride (C ₂₀ H ₃₈ O ₃)
Carbon, percent-----	75.13	74.4
Hydrogen, percent-----	11.12	11.0
Oxygen, percent-----	13.75	14.6
Bromine No.-----	3	0

Infrared analysis shows the presence of paraffin chains and cyclic anhydride structures.

EXAMPLE II

The production of methylcyclopentyl succinic anhy-

EXAMPLE III

This example illustrated the production of methylcyclohexyl succinic anhydride by the reaction of methylcyclohexane with maleic anhydride.

The charge to the bomb consisted of:

Methylcyclohexane, g----- 1000
Maleic anhydride, g----- 100
Di-tert-butylperoxide, g----- 20

The conditions were the same as in the previous experiment, that is, a temperature of 320° F. for 12 hours. On opening the bomb, 93 g. of solid and 920 g. of liquid product were found. The liquid on distillation yielded 74 g. of bottom product which was found to be readily soluble in benzene and analyzed as follows:

	Found	Theory For Methylcyclohexyl Succinic Anhydride (C ₁₁ H ₁₈ O ₃)
Carbon, percent-----	66.24	67.34
Hydrogen, percent-----	8.31	8.16
Oxygen, percent-----	25.45	24.50

The following table lists experimental data obtained in the preparation of alkyl and cycloalkyl succinic anhydride in accordance with the process of the invention.

Table

REACTION OF MALEIC ANHYDRIDE WITH SATURATED HYDROCARBONS

Hydrocarbon	Initiator	Solvent	Parts by Weight				Temp., ° F.	Yield Adduct, Percent ²
			Hydrocarbon	MA ¹	Initiator	Solvent		
2,3-dimethylbutane-----	DTBP ³	None-----	100	23	5.8	-----	284	25
Cetane-----	None-----	do-----	100	10	-----	-----	572	6
Do-----	None-----	do-----	100	10	-----	-----	600	10
Do-----	BP ⁴	do-----	100	10	1.0	-----	222	2
Do-----	DTBP	Benzene-----	100	5	0.62	100	284	12
Do-----	DTBP	do-----	100	5	1.25	100	284	19
Do-----	DTBP	None-----	100	10	2.0	-----	320	6
Do-----	DTBP	do-----	100	19.6	5.0	-----	284	12
Ethylated Wax ⁶ -----	DTBP	do-----	100	10	1.0	-----	320	20
Cyclopentane-----	DTBP	Benzene-----	100	5	1.25	100	284	Low
Methylcyclopentane-----	TBHP ⁵	None-----	100	10	2.0	-----	320	14
Do-----	DTBP	do-----	100	10	2.0	-----	320	37
Do-----	DTBP	do-----	100	10	2.0	-----	320	33
Cyclohexane-----	DTBP	do-----	100	10	2.0	-----	320	Low
Methylcyclohexane-----	DTBP	do-----	100	10	2.0	-----	320	34

¹ MA = maleic anhydride.

² Based on maleic anhydride charged.

³ DTBP = Di-tert-butylperoxide.

⁴ BP = benzoyl peroxide.

⁵ TBHP = Tert-butyl hydroperoxide.

⁶ Paraffin wax reacted with ethylene to yield branched chain liquid hydrocarbon of about 450 molecular weight.

dride by the reaction of methylcyclopentane with maleic anhydride was illustrated by this example.

The experiment was carried out as in the previous example charging the following materials to the bomb:

Methylcyclopentane, g----- 1000
Maleic anhydride, g----- 100
Di-tert-butylperoxide, g----- 20

In this case, the temperature was maintained at 320° F. for 12 hours. As in the previous experiment, most of the liquid material in the bomb was unreacted hydrocarbon but on distillation yielded 69 g. of reaction product. This was analyzed with the following results:

	Found	Theory For Methylcyclopentyl Succinic Anhydride (C ₁₀ H ₁₆ O ₃)
Carbon, percent-----	65.94	65.9
Hydrogen, percent-----	7.68	7.74
Oxygen, percent-----	26.38	26.3
Molecular Weight-----	185	182

The above test data show the efficacy of the reaction of alkanes and cycloalkanes with maleic anhydride in accordance with the process of this invention with representative alkanes and cycloalkanes containing from 6 to 32 carbon atoms. Better yields are obtained with branched chain hydrocarbons than with hydrocarbons containing no substituents. Ditertiarybutyl peroxide is shown to be outstanding as the catalyst in the above reaction.

I claim:

1. A process for preparing alkyl succinic acid anhydrides and cycloalkyl succinic acid anhydrides which comprises reacting a molar excess of a member of the group consisting of alkanes and cycloalkanes of from 6 to 32 carbon atoms with maleic anhydride in a closed system under autogenous pressure at a temperature from about 220° F. to about 400° F. and in the presence of ditertiary butyl peroxide free radical initiator catalyst.

2. A process for preparing cetyl succinic acid anhydride which comprises reacting a molar excess of cetane with maleic anhydride in a closed system under autogenous pressure at a temperature from about 220° F. to about

400° F. and in the presence of ditertiarybutyl peroxide catalyst.

3. A process for preparing methylcyclopentyl succinic acid anhydride which comprises reacting in a molar excess of methylcyclopentane with maleic anhydride in a closed system under autogenous pressure at a temperature from about 220° F. to about 400° F. and in the presence of ditertiarybutyl peroxide catalyst.

4. A process for preparing methylcyclohexyl succinic acid anhydride which comprises reacting a molar excess of methylcyclohexane with maleic anhydride in a closed system under autogenous pressure at a temperature from about 220° F. to about 400° F. in the presence of ditertiarybutyl peroxide catalyst.

5. A process for preparing a long chain alkyl succinic acid anhydride which comprises reacting a molar excess of a liquid branched chain ethylated paraffin wax having a molecular weight of about 450 with maleic anhydride in a closed system under autogenous pressure at a temperature from about 220° F. to about 400° F. in the presence of ditertiary butyl peroxide catalyst.

6. A process for the preparation of 2,3-dimethylbutylsuccinic anhydride which comprises reacting one mole of maleic anhydride with more than one mole of 2,3-dimethylbutane at a temperature of about 140° C. in a closed system under autogenous pressure with a catalytic amount of ditertiarybutyl peroxide.

7. A process for the preparation of alkyl hydrocarbon and cycloalkyl hydrocarbon substituted succinic acid an-

hydrides which comprises reacting one mole of maleic anhydride with more than one mole of a hydrocarbon selected from the group consisting of alkyl and cycloalkyl hydrocarbons at a temperature above 100° C. and in the presence of a catalytic amount of organic peroxide.

8. A process for the preparation of alkyl hydrocarbon and cycloalkyl hydrocarbon substituted succinic acid anhydrides which comprises reacting one mole of maleic anhydride with more than one mole of hydrocarbon selected from the group consisting of alkyl and cycloalkyl hydrocarbons of from 6 to 32 carbon atoms at a temperature above 100° C. and in the presence of a catalytic amount of organic peroxide.

9. A process for the preparation of alkyl hydrocarbon and cycloalkyl hydrocarbon substituted succinic acid anhydrides which comprises reacting one mole of maleic anhydride with more than one mole of hydrocarbon selected from the group consisting of alkyl and cycloalkyl hydrocarbons of from 6 to 32 carbon atoms at a temperature above 100° C. and in the presence of a catalytic amount of ditertiarybutyl peroxide.

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