3310K

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Patents Act

DECLARATION FOR A PATENT APPLICATION

▼ **INSTRUCTIONS**

(a) Insert "Convention" if applicable

(b) Insert FULL name(s) of applicant(s)

In support of the (a) Convention application made by (b) EASTMAN KODAK COMPANY

(c) Insert "of addition" if applicable

(d) Insert TITLE of invention

(hereinafter called "applicant(s)") for a patent (c) for an invention entitled (d)

PROCESS FOR THE PREPARATION OF ALKYL 3-ALKOXYPROPIONATES

(e) Insert FULL name(s) AND address(es) of declarant(s) (See headnotes)

I/We (e) Thomas F. Kirchoff, Patent Department, of EASTMAN KODAK COMPANY, 343 State Street, Rochester, New York, 14650, United States of America

do solemnly and sincerely declare as follows:

~~1. I am/We are the applicant(s).~~

(or, in the case of an application by a body corporate)

1. I am/~~We are~~ authorized to make this declaration on behalf of the applicant(~~s~~).

~~2. I am/We are the actual inventor(s) of the invention.~~

(or, where the applicant(s) is/are not the actual inventor(s))

(f) Insert FULL name(s) AND address(es) of actual inventor(s)

2. (f) Glenn Clark Jones of 3620 Hemlock Park Drive, Kingsport, Tennessee; William Dell Nottingham of 4700 Lakepark Drive, Kingsport, Tennessee and Peter Webb Raynolds of 720 Foothill Road, Kingsport, Tennessee. All respectively in the United States of America.

(g) Recite how applicant(s) derive(s) title from actual inventor(s) (See headnotes)

~~is~~/are the actual inventor(s) of the invention and the facts upon which the applicant(~~s~~) is/~~are~~ entitled to make the application are as follows:

(g) EASTMAN KODAK COMPANY is the assignee of the said invention from the actual inventor(s).

*(**Note**: Paragraphs 3 and 4 apply **only** to Convention applications)*

(h) Insert country, filing date, and basic applicant(s) for the/or EACH basic application

3. The basic application(~~s~~) for patent or similar protection on which the application is based is/~~are~~ identified by country, filing date, and basic applicant(~~s~~) as follows:

(h) United States of America on 07 March 1988

By Glenn Clark Jones
William Dell Nottingham
Peter Webb Raynolds

4. The basic application(~~s~~) referred to in paragraph 3 hereof was/~~were~~ the first application(~~s~~) made in a Convention country in respect of the invention the subject of the application.

(k) Insert PLACE of signing

(l) Insert DATE of signing

Declared at (k) Rochester, New York

Dated (l)

(12) PATENT ABRIDGMENT (11) Document No. AU-B-33504/89
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PROCESS FOR THE PREPARATION OF ALKYL 3-ALKOXYPROPIONATES

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(56) Prior Art Documents
US 2876239
FR 1233271

(57) Claim

1. Process for the preparation of an alkyl 3-alkoxypropionate which comprises reacting at a temperature of 10 to 50°C a dialkoxymethane with a ketene in the presence of a catalytic amount of methanedisulfonic acid, methanetrisulfonic acid or mixtures thereof.

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With international search report.

(54) Title: PROCESS FOR THE PREPARATION OF ALKYL 3-ALKOXYPROPIONATES

(57) Abstract

Disclosed is an improved process for the preparation of alkyl 3-alkoxypropionates by the reaction of a dialkoxymethane with a diketene in the presence of methanedisulfonic acid, methanetrisulfonic acid or mixtures thereof.

Description

Process for the Preparation of Alkyl 3-Alkoxypropionates

This invention concerns a novel process for the preparation of ether-ester compounds especially useful as solvents in the formulation of coating compositions. More particularly, this invention concerns a novel process for the preparation of alkyl 3-alkoxypropionates by the reaction of a dialkoxymethane with a ketene in the presence of certain di- and tri-sulfonic acids.

The synthesis of alkyl 3-alkoxypropionates by the reaction of a dialkoxymethane with a ketene is well known in the literature as shown by U.S. Patents 2,436,286, 2,910,503 and 3,052,713 and Chem. Listy, 47, 413 (1953) abstracted at C.A. 49:175C. Although the cited references suggest that various proton and Lewis acids may be used to catalyze the reaction, only the use of boron trifluoride and zinc chloride have been shown to effect the formation of alkyl 3-alkoxypropionates to any significant degree. Although useful in the reaction, boron trifluoride is expensive and presents corrosion, toxicity and waste disposal problems as compared to most proton acids. Zinc chloride is a poor catalyst for the reaction and also poses disposal problems. Two other Lewis acids have been found to be unsatisfactory. Boron triacetate is inactive while the extremely active aluminum chloride gives a complex mixture of products at low conversion.

U.S. Patent 2,436,286 mentions specifically the use of benzenesulfonic acid as a catalyst in the reaction of a dialkoxymethane compound with a ketene although no results are given with respect to its

use. We have found that benzenesulfonic acid is essentially inactive, especially in catalyzing reactions employing diethoxymethane or higher dialkoxymethanes. Methanesulfonic acid and a sulfonic acid ion exchange resin (Amberlyst 15) were found to be similar in activity to benzenesulfonic acid. Arylpolysulfonic acids were found to have insufficient catalytic activity with 1,3- and 1,4-benzenedisulfonic acids having poor activity and 1,2-benzenedisulfonic acid and 1,3,5-benzenetrisulfonic acid having only fair activity.

We have discovered that methanedisulfonic and methanetrisulfonic acids are excellent catalyst for the preparation of alkyl 3-alkoxypropionates by the reaction of a dialkoxymethane with a ketene according to known procedures. The activity of such acidic catalysts in the manufacture of alkyl 3-alkoxypropionates is good to excellent and their use does not involve any unusual disposal or toxicity problems. Furthermore, the methanepolysulfonic acid catalysts employed in our novel process are relatively inexpensive and require no unusual handling procedures. While the methanepolysulfonic acids, as well as certain other acidic compounds referred to hereinabove, are characterized as catalysts for the reaction, they are partially consumed in the process of preparing the alkyl 3-alkoxypropionates, i.e., all catalysts acidic enough to cause a reaction also react to some extent with the dialkoxymethane reactant or alcohol derived therefrom to give inactive esters or complexes. However, if desired unreacted catalyst may be recycled. For example, the distillation residue, resulting from the distillative isolation of the alkyl 3-alkoxypropionate from the crude product

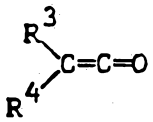
initially obtained from the process, may be recycled to the reactor to which the ketene and dialkoxymethane are fed.

The process of our invention involves the preparation of alkyl 3-alkoxypropionates by reacting a dialkoxymethane with a ketene in the presence of a catalytic amount of methanedisulfonic acid, methanetrisulfonic acid or a mixture thereof. The reactants and reaction conditions involved in the process of the invention are well known as shown by the references cited hereinabove. The dialkoxymethane reactant has the structure

$$R^1OCH_2OR^2$$

wherein R^1 and R^2 are the same or different alkyl groups, e.g., alkyl containing up to about eight carbon atoms. Typically, R^1 and R^2 represent the same alkyl groups of up to about four carbon atoms such as methyl, ethyl, propyl, isopropyl, butyl and isobutyl. Preferably, R^1 and R^2 are both ethyl.

The ketene compounds which may be used in the process have the general formula



wherein R^3 and R^4 are hydrogen or the same or different substituent selected from alkyl or aryl groups. In addition to the substituents which R^3 and R^4 may represent individually, they also may represent collectively alkylene groups such as pentamethylene, hexamethylene, oxadiethylene, thiadiethylene, etc. Typical alkyl and aryl groups represented by R^3 and R^4 are methyl, ethyl,

propyl, isopropyl, butyl, isobutyl, phenyl and p-tolyl. The preferred reactant is ketene, i.e., wherein each of R^3 and R^4 is hydrogen.

The temperature at which our novel process may be carried out normally should be in the range of about 10 to 50°C. Operating at temperatures outside of this range gives poor reaction rates and/or poor yields due to the conversion of the ketene to other products or decomposition of the dialkoxymethane reactant. The ratio of the reactants is not important although the process normally is performed using a stoichiometric excess of the dialkoxymethane reactant to avoid dimerization and polymerization of the ketene reactant. The ratio of reactants present in the reactor at any given time is difficult to determine at any given time because of their reactivity. When the process is conducted in a batch manner the ketene reactant generally is added over a period of time to a mixture of the catalyst in a dialkoxymethane. The ketene addition may be continuous or semi-continuous and should be at a rate sufficient to provide an acceptable conversion of the ketene to the desired alkyl alkoxypropionate product. When performing the process in a continuous manner a stream of a dialkoxymethane containing the catalyst is combined and mixed with a stream of the ketene reactant. The mole ratio of dialkoxymethane to ketene fed to the reactor regardless of the mode of operation may be in the range of about 1:1 to 20:1 although ratios in the range of about 1:1 to about 2:1 normally are used to maximize the conversion of the dialkoxymethane and thereby avoid the disposal or recycle of it.

The methanepolysulfonic acids used as catalysts in the process provided by our invention are known

materials and may be purchased or prepared according to published procedures. Methanedisulfonic acid may be prepared according to the procedures described in U.S. Patent 2,842,589 and in Rec. Des. Trav. Chim. Des. Pay-Bas, 48:949 (1929). Essentially pure methanetrisulfonic acid can be obtained by heating acetic anhydride and 65% oleum and recrystallizing the crude product obtained from water as described in U.S. Patent 2,333,701 (1943). Crude methanetrisulfonic acid may be obtained by heating a mixture of acetic acid with 65% oleum, also as disclosed in U.S. Patent 2,333,701. The pure methanepolysulfonic acids exist as hydrates, with one water molecule for each sulfonic acid group. Purchased methanetrisulfonic acid (Custom ChemLabs, Livermore, CA) was found to contain a mixture of methanedisulfonic acid and methanetrisulfonic acid in a di:tri weight ratio of approximately 1:2. We have found that at least some of the materials prepared according to U.S. Patent 2,333,701 and characterized as methanetrisulfonic acid actually contain from minor to significant amounts of catalytically-active methanedisulfonic acid and other unidentified products.

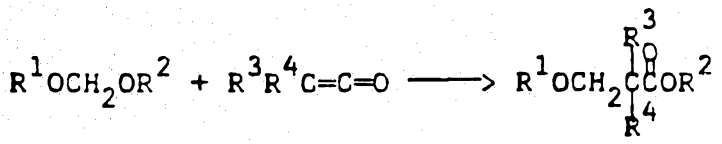
The amount of methanepolysulfonic acid which is catalytically effective in the process provided by our invention can be varied substantially depending, for example, on the activity of the particular methanepolysulfonic acid used, the design of the reactor or reactors, the ratio of reactants, the rate and degree of conversion desired, etc. Typically, about 0.005 to 0.5 weight percent of the methanepolysulfonic acid based on the weight of the dialkoxymethane reactant will be catalytically effective with amounts in the range of about 0.01 to 0.2 weight percent being preferred. The term

"catalyst" is used herein with the understanding that at least some of the catalyst is consumed during the operation of the process.

We have found that methanetrisulfonic acid, both in pure or crude form, e.g., methanetrisulfonic acid containing minor to significant amounts of methane-disulfonic acid and unknown reaction product, is especially active in catalyzing the reaction of a ketene with a dialkoxymethane to obtain an alkyl 3-alkoxypropionate. Thus, a particularly preferred embodiment of our invention comprises carrying out the process in the presence of methanetrisulfonic acid in a concentration of about 0.005 to 0.10, preferably 0.03 to 0.05, weight percent based on the weight of the dialkoxymethane reactant.

The process may be carried out in a batch, semi-continuous or continuous manner. A preferred mode of operation involves a counter-current absorber-reactor wherein the dialkoxymethane compound and catalyst are fed to the upper portion of a packed column and the ketene is fed to the lower portion. As the ketene gas contacts the mixture of dialkoxy-methane and catalyst it dissolves in and reacts with the dialkoxymethane to produce the alkyl 3-alkoxy-propionate product which is removed from the bottom of the column along with excess dialkoxymethane, any unreacted ketene and catalyst as well as by-products. The column underflow may be refined directly, for example, by distillation with or without prior neutralization. If the column under-flow contains a significant amount of ketene, the underflow may be fed to one or more hold-tanks to permit complete reaction of the ketene prior to purifying the crude reaction mixture.

The primary reaction which occurs during the process is represented by the equation:



wherein R^1, R^2, R^3 and R^4 are defined herein-above. When R^1 and R^2 represent different alkyl groups, the product will be a mixture of two or more compounds.

The process is particularly useful for the preparation of ethyl 3-ethoxypropionate by the reaction of diethoxymethane (R^1=R^2=ethyl) with ketene (R^3=R^4=hydrogen).

Our novel process is further illustrated by the following examples.

EXAMPLES 1-7.

A weighed amount of dimethoxymethane (DMM, Examples 1-3) or diethoxymethane (DEM, Examples 4-7) and catalyst is placed in a magnetically-stirred, three-neck flask equipped with a thermometer, gas inlet tube above the liquid surface and a dry ice condenser. Ketene is added over the surface of the dialkoxymethane reactant with a nitrogen flow from a diketene cracking furnace. Excess ketene is used due to some being lost through the condenser. The temperature is controlled between 25 and 40°C by the rate of ketene addition which is completed in one to two hours. When the exotherm stops, ketene addition is stopped and the reaction mixture is allowed to come to 25°C. After 30 minutes at 25°C, the reaction mixture is sampled for gas chromatography (GC) analysis. In Examples 1 and 2, 2.0 g decane are used as a GC Internal Standard.

In Example 1 the catalyst used is methane-disulfonic acid (MDSA) obtained from dichloromethane

and potassium sulfite according to the procedure described in Rec. Des. Trav. Chim. Des. Pay-Bas, 48:949 (1929). The pure methanetrisulfonic acid (MTSA-R) used in Examples 2 and 5 is prepared from 65% oleum (65% free sulfur trioxide in sulfuric acid) and acetic anhydride according to the procedure disclosed in U.S. Patent 2,333,701. The crude methanetrisulfonic acid obtained is purified by dissolving in a minimum amount of water and heating to 50°C, adding activated charcoal and a filtering aid and filtering. The water in the filtrate is stripped under vacuum and the recrystallized MTSA is dried in a vacuum oven at 75°C and 20 inches Hg pressure.

The crude methanetrisulfonic acid (MTSA-C) used without purification in Examples 3 and 6 is prepared fom 65% oleum and acetic acid according to the procedure of U.S. Patent 2,333,701. The methanetrisulfonic acid (MTSA-P) used in Example 7 is obtained from Custom ChemLabs. The purchased methanetrisulfonic acid consisted of a mixture of methanedisulfonic acid and methanetrisulfonic acid in a weight ratio of di-tri of approximately 1:2. The methanedisulfonic acid (MDSA-P) used in Example 4 was purchased from Kodak Laboratory Chemicals in the form of a 50% aqueous solution. The MDSA-P used was obtained by removing the water under vacuum.

The following Table shows the amounts (g) of catalyst and dialkoxymethane (DAM) reactant used, the amount (moles) of ketene added, and the amounts (g) of unreacted DAM reactant and alkyl 3-alkoxypropionate (AAP) product obtained in each of Example 1-7. In Examples 4 and 5 the DEM used has a very high purity of 99.99% DEM with 0.01% water. In the other examples the DAM reactant has a purity of

approximately 99.9% with 0.1% water. MMP and EEP designate methyl 3-methoxypropionate and ethyl 3-ethoxypropionate, respectively.

TABLE

Example	Catalyst	DAM Rectant	AAP Product	Ketene Added	Unreacted DAM
1	MDSA 0.071	DMM 23.0	MMP 24.9	0.30	DMM 2.4
2	MTSA-R 0.005	DMM 23.0	MMP 13.5	0.16	DMM 10.3
3	MTSA-C 0.012	DMM 40.0	MMP 38.3	0.46	DMM 15.8
4	MDSA-P 0.060	DEM 50.0	EEP 62.0	0.61	DEM 2.9
5	MTSA-R 0.010	DEM 50.0	EEP 49.7	0.49	DEM 13.9
6	MTSA-C 0.007	DEM 42.0	EEP 26.2	0.26	DEM 21.6
7	MTSA-P 0.020	DEM 40.0	EEP 43.0	0.42	DEM 5.6

EXAMPLE 8

A. Dimethoxymethane (381 g, 5.0 mol) and pure methanetrisulfonic acid (0.148 g) are charged to a one liter, magnetically-stirred, three-neck flask equipped with a thermometer, gas inlet tube and a dry ice condenser. Ketene is added over the surface of the dimethoxymethane with a nitrogen flow from a diketene cracking furnace. The reaction mixture is cooled externally to maintain a temperature of 40°C while adding the ketene as fast as possible. Ketene addition is terminated when the exotherm stops and a sample of the reaction mixture is analyzed by GC.

The reaction mixture consisting of 87% methyl 3-methoxypropionate, 8% dimethoxymethane and 5% other compounds is vacuum distilled through a 10 plate Oldershaw column at 30 Torr and 57°C to recover methyl 3-methoxypropionate (505 g, 4.28 mol) and unreacted dimethoxymethane (31 g, 0.4 mol).

B. Procedure A is repeated using dimethoxymethane (152 g, 2.0 mol) and the black, liquid distillation residue (13 g) resulting from Procedure A. GC analysis of the reaction mixture shows that it consists of 87.3% methyl 3-methoxypropionate, 5.8% dimethoxymethane and 6.9% other material. Vacuum distillation of the reaction mixture gives methyl 3-methoxypropionate (201 g, 1.7 mol) and dimethoxymethane (9.2 g, 0.12 mol) and a distillation residue of 20 g of black liquid. The 20 g distillation residue failed to catalyze the reaction of additional dimethoxymethane and ketene.

EXAMPLE 9

A. Example 8A is repeated using diethoxymethane (319 g, 3.06 mol) and crude methanetrisulfonic acid (0.220 g). GC analysis establishes that the resulting reaction mixture consists of 83% ethyl 3-ethoxypropionate, 9% diethoxymethane and 8% other material. Vacuum distillation of the reaction mixture at 25 Torr through a 10 plate Oldershaw column gives ethyl 3-ethoxypropionate (357.8 g, 2.45 mol) and diethoxymethane (32.5 g, 0.31 mol). The distillation residue consisted of 20 g of black liquid.

B. Example 8A is repeated using diethoxymethane (312 g, 3.0 mol) and the distillation residue of Example 9A. Vacuum distillation of the reaction mixture thus obtained gives ethyl 3-ethoxypropionate

(170 g, 1.16 mol) and unreacted diethoxymethane (188 g, 1.8 mol).

While the invention has been described in detail with particular reference to preferred embodiments thereof, it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

Claims

We Claim:

1. Process for the preparation of an alkyl 3-alkoxypropionate which comprises reacting at a temperature of 10 to 50°C a dialkoxymethane with a ketene in the presence of a catalytic amount of methanedisulfonic acid, methanetrisulfonic acid or mixtures thereof.

2. Process for the preparation of an alkyl 3-alkoxypropionate having the formula

$$R^1OCH_2CH_2\overset{O}{\overset{\|}{C}}OR^2$$

which comprises reacting a dialkoxymethane having the formula $R^1OCH_2OR^2$ with ketene at a temperature of 10 to 50°C in the presence of a catalytic amount of methanetrisulfonic or a mixture of methanetrisulfonic acid and methanedisulfonic acid, wherein R^1 and R^2 each is alkyl of up to ~~about~~ 4 carbon atoms.

3. Process according to Claim 2 wherein the process is carried out in the presence of 0.005 to 0.10 weight percent methanetrisulfonic acid or a mixture of methanetrisulfonic acid and methanedisulfonic acid based on the weight of the dialkoxymethane reactant.

4. Process for the preparation of an alkyl 3-alkoxypropionate having the formula

$$R^1OCH_2CH_2\overset{O}{\overset{\|}{C}}OR^2$$

which comprises reacting a dialkoxymethane having the formula $R^1OCH_2OR^2$ with ketene at a temperature of 10 to 50°C in the presence of 0.01 to 0.20 weight percent, based on the weight of the dialkoxymethane, methanetrisulfonic acid; wherein each R^1 and R^2 is methyl or ethyl.

5. A process according to claim 1 substantially as hereinbefore described with reference to any one of the examples.

DATED: 24 January 1991

PHILLIPS ORMONDE & FITZPATRICK
Attorneys for:
EASTMAN KODAK COMPANY

David B Fitzpatrick

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 89/00763

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) [5]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC[4]: C 07 C 69/708; C 07 C 67/46

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC[4]	C 07 C 69/00; C 07 C 67/00

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category [10]	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
A	US, A, 2876239 (A.E. MONTAGNA) 3 March 1959, see column 1, lines 23-38 --	1
A	FR, A, 1233271 (WACKER-CHEMIE) 12 October 1960, see page 1, right-hand column, last three paragraphs; page 3, left-hand column, table ----	1

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
17th May 1989	14. 06. 89
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	P.C.G. VAN DER PUTTEN

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. US 8900763 SA 27266

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 07/06/89
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 2876239		None	
FR-A- 1233271		CH-A- 389583	
		CH-A- 417561	
		DE-B- 1067798	
		GB-A- 923341	
		GB-A- 923342	
		US-A- 3049560	
		US-A- 3134807	