

Description

This invention concerns mercaptoalkyl acetoacetates, use thereof as chain transfer agents and a process for the preparation of mercaptoalkyl acetoacetates. More particularly, this invention concerns mercaptoalkyl acetoacetates which may be effective chain transfer agents in free-radical polymerization reactions. The mercaptoalkyl acetoacetates may function as chain transfer agents and thereby introduce reactive acetoacetate functional endgroups into at least some of the polymer molecules so prepared. The process encompasses the reaction of TKD, a diketene-acetone adduct, namely, 2,2,6-trimethyl-1,3-dioxen-4-one, with hydroxy-functional mercaptans. The process may produce superior yields of the pure mercaptoalkyl acetoacetates relative to the corresponding reaction with diketene.

Miles and Owen (L.W.C. Miles and L.N. Owen, J. Chem. Soc., 817-826 (1952)) disclose a process for preparing 2-mercaptoethyl acetate by direct acetylation of 2-mercaptoethanol with acetic anhydride.

It has long been known that aliphatic, cycloaliphatic, or aromatic compounds containing hydroxyl groups can react with diketene to produce acetoacetic esters. The catalytic use of acid-base couples of acetic acid and tertiary aliphatic amines is disclosed in US-A-2 351 366.

The reaction of diketene with hydroxyl groups is also disclosed in US-A-3 542 855. The process for the preparation of acetoacetic esters by reacting diketene with a mono-, di-, or tri-hydric aliphatic alcohol having 1 to 18 carbon atoms in the presence of certain levels of certain tertiary diamines is disclosed.

Carroll and Bader (M.F. Carroll and A.R. Bader, J. Am. Chem. Soc., Vol. 75, 5400-5402(1953)) disclose the acid-catalyzed reactions of diketene with ketones which yielded 2,2-disubstituted-4-methyl-6-keto-1,3-dioxenes, many reactions of which dioxenes paralleled those of diketene. The adduct of diketene with acetone yielded 2,2,6-trimethyl-1,3-dioxen-4-one (TKD); the reactions of TKD with methanol or 1-butanol to yield methyl acetoacetate or n-butyl acetoacetate are exemplified.

Clemens and Hyatt (R.J. Clemens and J.A. Hyatt, J. Org. Chem., Vol. 50, 2431-2435(1985)) disclose some of the deficiencies of acetoacetylation of nucleophiles with diketene, a highly reactive, lacrymatory, and toxic reagent. They disclose rapid acetoacetylation of a series of aliphatic alcohols with TKD which proceeded with excellent yield and provided product of excellent purity. They further disclose that thiophenol and two aliphatic mercaptans are acetoacetylated in good yield (using TKD). They also allege that "this acetoacetylation process (using TKD and mercaptan) is probably the method of choice for preparing thioacetoacetate esters". However, they exemplify the reaction of TKD with thiophenol to yield a 72% yield of thiophenyl acetoacetate, not the thioacetoacetate discussed in the reference, such as, for example, hydroxyphenyl thioacetoacetate. The teaching of the Clemens and Hyatt article with respect to formation of thioacetoacetates is incomplete and unclear. Further, this teaching is not resolved by our Comparative Example directed to this reaction.

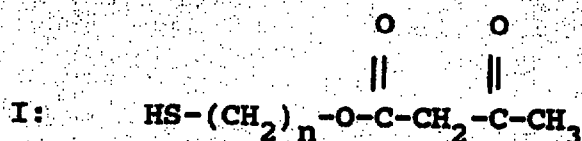
US-A-3 689 568 discloses a process for preparing primary mercaptans which comprises reacting hydrogen sulfide with certain alpha-olefins and a certain trivalent organic phosphorous initiator under certain conditions. Generically disclosed, but not exemplified or claimed as olefin reactants are vinyl esters. There is no suggestion, however, of vinyl acetoacetate as an alpha-olefin to be used in the process disclosed nor does the disclosure direct one to try a vinyl ester of a multi-functional carboxylic acid.

This invention relates to mercaptoalkyl acetoacetates and a process for the preparation of mercaptoalkyl acetoacetates. This invention also relates to the process of reacting mercaptoalkanols with a diketene-ketone adduct such as, for example, TKD, 2,2,6-trimethyl-1,3-dioxen-4-one, at a temperature at least high enough to cause the decomposition of the diketene-ketone adduct in order to produce high yields of mercaptoalkyl acetoacetates.

This invention also relates to mercaptoalkyl acetoacetates which function as chain transfer agents in free radical polymerization reactions. With the primary chain transfer reaction involving the mercapto group of the mercaptoalkyl acetoacetates, at least some of the polymer chains produced in the free radical polymerization reaction contain acetoacetate functionality incorporated into the formed polymer.

In accordance with the present invention, we provide mercapto-(C₁-C₈)alkylacetoacetates. The alkyl group may be substituted or unsubstituted and may be linear or branched. Preferably, the C atom of the alkyl group which connects directly with the acetoacetate group is unsubstituted. Preferred compounds are mercapto-(C₁-C₃)alkylacetoacetates, the mercapto-(C₂)alkylacetoacetates being the most preferred. When the compounds of the present invention are substituted, the substituent(s) preferably will not inhibit any chain transfer agent properties the corresponding unsubstituted compound may possess. The preferred compounds of the present invention include mercaptomethylacetoacetate, mercaptoethylacetoacetate, mercaptopropylacetoacetate, mercaptobutylacetoacetate, mercaptopentylacetoacetate, mercaptohexylacetoacetate, mercaptooctylacetoacetate and branched isomers thereof, such as mercaptisobutylacetoacetate.

The new class of compounds preferably have the Formula:



wherein n is 1 to 8. Preferably, the C atom of the (CH₂)_n radical adjacent to the O atom is unsubstituted. More preferably, n in the Formula I is from 1 to 3. Most preferably n in the Formula I is 2.

In another aspect, the present invention concerns a process for the preparation of mercaptoalkyl acetoacetates, for example mercapto(C₁-C₈)alkyl acetoacetates. The process comprises contacting a mercaptoalkanol, for example a mercapto-(C₁-C₈) alkenol with TKD at a temperature sufficient to cause decomposition of TKD. A temperature in the range of from 80°C. to 170°C is preferably employed. In the most preferred embodiment of this invention temperatures of from 110°C to 130°C are employed.

In yet another aspect, the present invention concerns the use of mercapto(C₁-C₈)alkyl acetoacetates as chain transfer agents in free radical addition polymerization reactions. These reactions embrace the preparation of oligomers and polymers by the free radical polymerization of ethylenically unsaturated monomers in solution in substantially aqueous media or in organic solvent media; in bulk; or in emulsion, dispersion or suspension form in substantially aqueous media, as, for example, in aqueous latex preparation, or in organic solvent media, as, for example, in non-aqueous dispersion preparation.

The following examples are intended to illustrate the subject compounds and the process for preparing the subject compounds to which this invention is directed. They are not intended to limit the invention as other applications of the invention will be obvious to those of ordinary skill in the art.

Example 1: Preparation of mercaptoethylacetoacetate

In a 300 ml. round bottom flask fitted with a thermometer, mechanical stirrer, Dean Stark trap and reflux condenser was placed 25.0g. (0.32 mole) of 2-mercaptoethanol. This was stirred and heated to 130°C.; 45.4g. (0.32 mole) of 2,2,6-trimethyl-1,3-dioxen-4-one (TKD) was added dropwise at a uniform rate over the period of one hour. Heating was continued for 1/2 hour; acetone distillate was collected in the Dean Stark trap. After distillate collection was completed, the mixture was distilled under vacuum and the portion boiling at 110°-115°C. (at 5 mm. Hg.) was collected to give a colorless liquid of mercaptoethylacetoacetate. The yield was about 90% based on starting material. The product was identified by NMR spectroscopy.

Example 2: Preparation of 3-mercapto-2-butylacetoacetate

The reaction of TKD with 3-mercapto-2-butanol was carried out according to the process of Example 1. The yield of the acetoacetate functional mercaptan was about 80%.

Comparative Example: Preparation of 4-hydroxyphenylthioacetoacetate or 4-mercaptophenyl acetoacetate

In a 500 ml. round bottom flask equipped with a nitrogen sparge, mechanical stirrer, condenser with Dean-Stark trap, and thermometer was placed 50.0g. (0.4 mole) hydroxythiophenol and 56.3g. TKD. The mixture was heated to 130°C. and acetone was collected in the trap. Heating was continued for two hours. The reaction mixture was analyzed by NMR; no starting material was present and little to none of either reaction product was found.

Example 4: Use of mercaptoethylacetoacetate as a chain transfer agent

In a 500ml. round bottom flask equipped with a thermometer, nitrogen sparge, mechanical stirrer and reflux condenser was placed 60.0g. of xylene. This was heated to 105°C with stirring. Two monomer solutions were separately premixed. The first contained 42.5g. of butyl methacrylate, 7.5g. of methyl methacrylate, and 9.2g. of mercaptoethylacetoacetate. The second mixture contained 42.5g. of butyl methacrylate, 7.5g. of methyl methacrylate, and 1.1g. of t-butyl peroctoate. The two solutions were pumped simultaneously into the xylene solution over a period of 0.8 hour. After 0.3 hr. of additional heating, in additional 0.2g. of t-butyl peroctoate was added and heating was continued for 0.5 hr. The heat was removed. The polymer solution was at 60.54 % solids content. Gel permeation chromatography molecular weights were Mw=3730 and Mn=1770, which

demonstrates the efficacy of the mercaptoethylacetoacetate as a chain transfer agent.

Claims

1. A process for preparing a mercaptoalkylacetoacetate comprising contacting a mercaptoalkanol with 2,2,6-trimethyl-1,3-dioxen-4-one at a temperature of from 80°C to 170°C.
2. A compound which is a mercapto(C₁-C₈)alkylacetoacetate.
3. A compound as claimed in claim 2, wherein the C atom of the alkyl group which connects directly with the acetoacetate group is unsaturated.
4. A compound as claimed in claim 2 or claim 3, wherein the compound is a mercapto(C₁-C₃)alkylacetoacetate, and is preferably a mercapto(C₂)alkylacetoacetate.
5. A compound as claimed in claim 2 or claim 3, which is mercapto methylacetoacetate, mercaptoethylacetoacetate, mercaptopropylacetoacetate, mercaptoethylacetoacetate, mercaptopentylacetoacetate, mercaptohexylacetoacetate, mercaptoheptylacetoacetate, mercaptooctylacetoacetate or a branched isomer thereof.
6. A process as claimed in claim 1 for preparing a compound as claimed in any one of claims 2-5, wherein the mercaptoalkanol is mercapto(C₁-C₈)alkanol.
7. A process as claimed in claim 1 or claim 6 wherein the process is carried out a temperature of from 110° to 130°C.
8. Use of a compound formed by the process of claim 1 as a claim transfer agent in a free radical polymerisation reaction.
9. Use of a compound as claimed in any one of claims 2-5 as a chain transfer agent in a free radical polymerisation reaction.

Patentansprüche

1. Verfahren zur Herstellung eines Mercaptoalkylacetoacetats, bei dem man ein Mercaptoalkanol mit 2,2,6-Trimethyl-1,3-dioxen-4-on bei einer Temperatur von 80°C bis 170°C in Kontakt bringt.
2. Verbindung, nämlich Mercapto(C₁-C₈)alkylacetoacetat.
3. Verbindung nach Anspruch 2, worin das mit der Acetoacetat-Gruppe direkt verbundene C-Atom der Alkyl-Gruppe ungesättigt ist.
4. Verbindung nach Anspruch 2 oder 3, worin die Verbindung ein Mercapto(C₁-C₃)alkylacetoacetat und vorzugsweise ein Mercapto(C₂)alkylacetoacetat ist.
5. Verbindung nach Anspruch 2 oder 3, nämlich Mercaptomethylacetoacetat, Mercaptoethylacetoacetat, Mercaptopropylacetoacetat, Mercaptoethylacetoacetat, Mercaptopentylacetoacetat, Mercaptohexylacetoacetat, Mercaptoheptylacetoacetat, Mercaptooctylacetoacetat oder ein verzweigtes Isomer davon.
6. Verfahren nach Anspruch 1 zur Herstellung einer Verbindung nach einem der Ansprüche 2 bis 5, worin das Mercaptoalkanol Mercapto(C₁-C₈)alkanol ist.
7. Verfahren nach Anspruch 1 oder 6, worin das Verfahren bei einer Temperatur von 110°C bis 130°C durchgeführt wird.
8. Verwendung einer durch das Verfahren nach Anspruch 1 gebildeten Verbindung als Ketten-Übertragungsmittel in einer Radikalketten-Polymerisationsreaktion.
9. Verwendung einer Verbindung nach einem der Ansprüche 2 bis 5 als Ketten-Übertragungsmittel in einer Radikalketten-Polymerisationsreaktion.

Revendications

1. Procédé de préparation d'un acétoacétate de mercaptoalkyle, qui consiste à faire réagir un mercaptoalkanol avec de la 2,2,6-triméthyl-1,3-dioxène-4-one à une température de 80 à 170°C.
2. Composé, qui est un acétoacétate de mercapto(alkyle en C₁-C₈).
3. Composé selon la revendication 2, dans lequel l'atome de carbone du groupe alkyle qui assure la liaison directe avec le groupe acétoacétate est non saturé.
4. Composé selon la revendication 2 ou la revendication 3, dans lequel le composé est un acétoacétate de mercapto(alkyle en C₁-C₃), de préférence un acétoacétate de mercapto(alkyle en C₂).
5. Composé selon la revendication 2 ou 3 qui est l'un des composés suivants : acétoacétate de mercap-



demonstrates the efficacy of the mercaptoethylacetoacetate as a chain transfer agent.

Claims

1. A process for preparing a mercaptoalkylacetoacetate comprising contacting a mercaptoalkanol with 2,2,6-trimethyl-1,3-dioxen-4-one at a temperature of from 80°C to 170°C.
2. A compound which is a mercapto(C₁-C₈)alkylacetoacetate.
3. A compound as claimed in claim 2, wherein the C atom of the alkyl group which connects directly with the acetoacetate group is unsaturated.
4. A compound as claimed in claim 2 or claim 3, wherein the compound is a mercapto(C₁-C₃)alkylacetoacetate, and is preferably a mercapto(C₂)alkylacetoacetate.
5. A compound as claimed in claim 2 or claim 3, which is mercapto methylacetoacetate, mercaptoethylacetoacetate, mercaptopropylacetoacetate, mercaptobutylacetoacetate, mercaptopentylacetoacetate, mercaptohexylacetoacetate, mercaptoheptylacetoacetate, mercaptooctylacetoacetate or a branched isomer thereof.
6. A process as claimed in claim 1 for preparing a compound as claimed in any one of claims 2-5, wherein the mercaptoalkanol is mercapto(C₁-C₈)alkanol.
7. A process as claimed in claim 1 or claim 6 wherein the process is carried out at a temperature of from 110° to 130°C.
8. Use of a compound formed by the process of claim 1 as a chain transfer agent in a free radical polymerisation reaction.
9. Use of a compound as claimed in any one of claims 2-5 as a chain transfer agent in a free radical polymerisation reaction.

Patentansprüche

1. Verfahren zur Herstellung eines Mercaptoalkylacetoacetats, bei dem man ein Mercaptoalkanol mit 2,2,6-Trimethyl-1,3-dioxen-4-on bei einer Temperatur von 80°C bis 170°C in Kontakt bringt.
2. Verbindung, nämlich Mercapto(C₁-C₈)alkylacetoacetat.
3. Verbindung nach Anspruch 2, worin das mit der Acetoacetat-Gruppe direkt verbundene C-Atom der Alkyl-Gruppe ungesättigt ist.
4. Verbindung nach Anspruch 2 oder 3, worin die Verbindung ein Mercapto(C₁-C₃)alkylacetoacetat und vorzugsweise ein Mercapto(C₂)alkylacetoacetat ist.
5. Verbindung nach Anspruch 2 oder 3, nämlich Mercaptomethylacetoacetat, Mercaptoethylacetoacetat, Mercaptopropylacetoacetat, Mercaptobutylacetoacetat, Mercaptopentylacetoacetat, Mercaptohexylacetoacetat, Mercaptoheptylacetoacetat, Mercaptooctylacetoacetat oder ein verzweigtes Isomer davon.
6. Verfahren nach Anspruch 1 zur Herstellung einer Verbindung nach einem der Ansprüche 2 bis 5, worin das Mercaptoalkanol Mercapto(C₁-C₈)alkanol ist.
7. Verfahren nach Anspruch 1 oder 6, worin das Verfahren bei einer Temperatur von 110°C bis 130°C durchgeführt wird.
8. Verwendung einer durch das Verfahren nach Anspruch 1 gebildeten Verbindung als Ketten-Übertragungsmittel in einer Radikalketten-Polymerisationsreaktion.
9. Verwendung einer Verbindung nach einem der Ansprüche 2 bis 5 als Ketten-Übertragungsmittel in einer Radikalketten-Polymerisationsreaktion.

Revendications

1. Procédé de préparation d'un acétoacétate de mercaptoalkyle, qui consiste à faire réagir un mercaptoalcool avec de la 2,2,6-triméthyl-1,3-dioxène-4-one à une température de 80 à 170°C.
2. Composé, qui est un acétoacétate de mercapto(alkyle en C₁-C₈).
3. Composé selon la revendication 2, dans lequel l'atome de carbone du groupe alkyle qui assure la liaison directe avec le groupe acétoacétate est non saturé.
4. Composé selon la revendication 2 ou la revendication 3, dans lequel le composé est un acétoacétate de mercapto(alkyle en C₁-C₃), de préférence un acétoacétate de mercapto(alkyle en C₂).
5. Composé selon la revendication 2 ou 3 qui est l'un des composés suivants : acétoacétate de mercap-



tométhyle, acétoacétate de mercaptoéthyle, acétoacétate de mercaptopropyle, acétoacétate de mercaptobutyle, acétoacétate de mercaptopentyle, acétoacétate de mercaptohexyle, acétoacétate de mercaptooctyle et leurs isomères ramifiés.

6. Procédé selon la revendication 1, destiné à préparer un composé selon l'une quelconque des revendications 2-5, dans lequel le mercaptoalcanol est un mercapto(alcanol en C_1-C_8).

7. Procédé selon la revendication 1 ou la revendication 6, dans lequel le procédé est mis à oeuvre à une température de 110 à 130°C.

8. Utilisation d'un composé obtenu par le procédé selon la revendication 1, en tant qu'agent de transfert de chaîne au cours d'une réaction de polymérisation radicalaire.

9. Utilisation d'un composé selon l'une quelconque des revendications 2 à 5 en tant qu'agent de transfert de chaîne au cours d'une réaction de polymérisation radicalaire.