PROCESS FOR PREPARING AN ALPHA-SUBSTITUTED ACRYLATE

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The present application claims benefit of priority to U.S. Application No. 62/954,941, filed on December 30, 2019, which is incorporated herein by reference in its entirety.

BACKGROUND

[0002] Alpha-substituted acrylates, such as alpha-(alkyl) acrylates or alpha-(polymeryl) acrylates, are important intermediates for preparing useful polymeric materials. Synthetic routes for the preparation of alpha-substituted acrylates and bisacrylates from organozinc reagents are known in the art. However, such routes employ transmetallation of organozinc compounds to organocopper compounds, and the direct reaction of organozinc compounds with halomethylacrylates is not known. The present disclosure addresses such a need by demonstrating a direct reaction of organozinc compounds with alpha-(halomethyl) acrylates to synthesize alpha-(alkyl) and alpha-(polymeryl) acrylates.

SUMMARY

[0003] The present disclosure is directed to a process for preparing an alpha-substituted acrylate, the process comprising:

a) combining starting materials comprising an alpha-(halomethyl) acrylate and an organozinc compound,

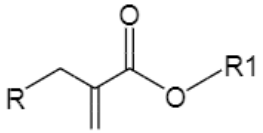
thereby forming a product comprising the alpha-substituted acrylate.

[0003a] In one aspect, the present disclosure is directed to a process for preparing an alpha-substituted acrylate, the process comprising:

a) combining starting materials comprising an alpha-(halomethyl) acrylate and an organozinc compound of the formula R_2Zn,

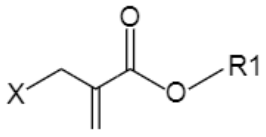
thereby forming a product comprising the alpha-substituted acrylate, wherein:

the alpha-substituted acrylate has the formula (I):



(I);

the alpha-(halomethyl) acrylate has the formula (II):



(II);

each R independently is a C1-C26 hydrocarbyl group or a polyolefinyl group;

each R1 independently is a C1-C30 hydrocarbyl group; and

X is a halogen,

wherein the process excludes any transmetallation step or reaction.

BRIEF DESCRIPTION OF DRAWINGS

[0004] FIGS. 1A and 1B provide the ^{1}H NMR and ^{13}C NMR spectra, respectively, for Example 1.

[0005] FIGS. 1C and 1D provide the GCMS spectra for Example 1.

[0006] FIG. 2 provides the NMR spectra for Example 2.

[0007] FIGS. 3A and 3B provide the NMR spectra for Example 3.

[0008] FIGS. 4A and 4B provide the NMR spectra for Example 4.

DETAILED DESCRIPTION

Definitions

[0009] All references to the Periodic Table of the Elements herein shall refer to the Periodic Table of the Elements, published and copyrighted by CRC Press, Inc., 2003.

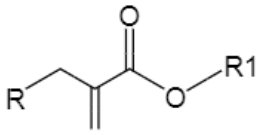
Claims:

1. A process for preparing an alpha-substituted acrylate, the process comprising:

a) combining starting materials comprising an alpha-(halomethyl) acrylate and an organozinc compound of the formula R_2Zn,

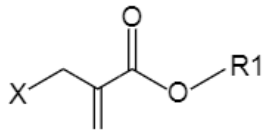
thereby forming a product comprising the alpha-substituted acrylate, wherein:

the alpha-substituted acrylate has the formula (I):



(I);

the alpha-(halomethyl) acrylate has the formula (II):



(II);

each R independently is a C1-C26 hydrocarbyl group or a polyolefinyl group;

each R1 independently is a C1-C30 hydrocarbyl group; and

X is a halogen,

wherein the process excludes any transmetallation step or reaction.

2. The process of claim 1, wherein the starting materials of step a) further comprise a solvent.

3. The process of claim 2, wherein the solvent is a non-aromatic hydrocarbon solvent.

4. The process of any of the previous claims, wherein the starting materials of step a) further comprise an organocatalyst.

5. The process of any of the previous claims, wherein each R independently is a C1-C26 hydrocarbyl group.

6. The process of any of claims 1-4, where each R independently is a polyolefinyl group, which can be defined by the properties of R-H, wherein R-H has a number average molecular weight of greater than 365 g/mol.

7. The process of claim 6, wherein the polyolefinyl group is an ethylene-based polymeryl group.

8. The process of claim 7, wherein the polyolefinyl group is an ethylene homopolymeryl group comprising units derived from ethylene.

9. The process of claim 7, wherein the polyolefinyl group is an ethylene/alpha-olefin interpolymeryl gruop comprising units derived from ethylene and a C3-C30 alpha-olefin.