United States Patent [19]

Inamoto et al.

[11] **3,818,069**

[45] **June 18, 1974**

[54] **ESTERS OF ADAMANTANE-1-ACETIC ACID**

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[22] Filed: **July 23, 1971**

[21] Appl. No.: **165,752**

[30] **Foreign Application Priority Data**

July 31, 1970 Japan 45-67203

[52] **U.S. Cl.** ..... **260/468 G,** 252/57

[51] **Int. Cl.** **C07c 69/74**

[58] **Field of Search** ..... 200/468 G, 468 CA

[56] **References Cited**

UNITED STATES PATENTS

3,591,642 7/1971 Szinai et al. 260/617

OTHER PUBLICATIONS

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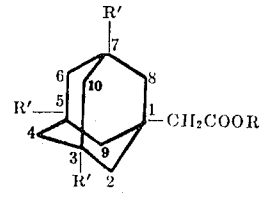
[57] **ABSTRACT**

A compound of the formula



wherein R is selected from the group of hydrocarbon radicals having 4 to 20 carbon atoms consisting of (a) linear and branch-chain alkyls and alkenyls, and (b) monocyclic and polycyclic cycloalkyls and cycloalkenyls; and R′ is H or alkyl having 1 to 4 carbon atoms, is prepared by reacting adamatane-1-acetic acid, or its alkyl derivatives, with a monohydric alcohol (ROH) in the presence of esterification catalyst. The compounds are useful as oiling agents for synthetic fibers and as synthetic lubricating oil bases.

2 Claims, No Drawings

ESTERS OF ADAMANTANE-1-ACETIC ACID

BACKGROUND OF THE INVENTION

1. FIELD OF THE INVENTION

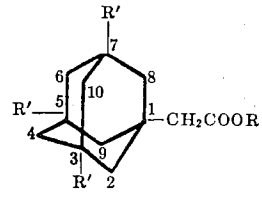
This invention relates to a process for preparing esters of adamantane-1-acetic acid. More particularly, it relates to a process for preparing esters of adamantane-1-acetic acid and alkyladamantane-1-acetic acid with higher alcohols having from 4 to 20 carbon atoms.

2. DESCRIPTION OF THE PRIOR ART

Among the esters of adamantane-1-acetic acid and ring-substituted alkyl derivatives thereof, only a few methyl esters such as methyl 3-methyladamantyl-1-acetate, methyl 3,5-dimethyladamantyl-1-acetate, etc. (K. Bott, Ber. 101, 564 (1968)) have been synthesized hitherto but higher esters with alcohols having more than four carbon atoms, have not been known.

SUMMARY OF THE INVENTION

According to the invention, there is provided a compound of the formula



wherein R is selected from the group of hydrocarbon radicals having 4 to 20 carbon atoms consisting of (a) linear and branch-chain alkyls and alkenyls, and (b) monocyclic and polycyclic cycloalkyls and cycloalkenyls; and R' is H or alkyl having 1 to 4 carbon atoms.

We have found that adamantane-1-acetic acid and its ring-substituted alkyl derivatives can be esterified with various higher alcohols according to known methods. Thus, the present invention provides a method of preparing the novel esters by the reaction of adamantane-1-acetic acid, or ring-substituted derivatives thereof, with straight-chain or branched-chain noncyclic or mono- or polycyclic alkanols or alkenols in the presence of an acid, neutral or basic catalyst.

These esters contain the adamantane ring which renders the molecule high thermal stability as well as providing many characteristic advantageous properties not encountered in usual fatty esters. Therefore, these novel esters are very useful as components of oiling agents for synthetic fibers, as synthetic lubricating oil bases, particularly for airplane usage, and for many other purposes.

The object of the present invention can be achieved by heating adamantane-1-acetic acid or ring-substituted alkyl derivatives thereof with the said higher alcohols in the presence of esterification catalysts. The effective catalysts to be used in the present reaction include acid catalysts such as sulfuric acid, aliphatic and aromatic sulfonic acids, boron trifluoride and the like, neutral or alkaline catalysts such as oxides or hydroxides of alkali metals, alkaline earth metals, zinc, cadmium, tin, lead, antimony, bismuth and the like, all the other known esterification catalysts being included.

Examples of the ring-substituted derivatives of adamantane-1-acetic acid are 3-methyl-, 3,5-dimethyl-, 3,5,7-trimethyl-, 3-methyl-5-ethyl-, 3,5-dimethyl-7-ethyl-, and 3-n-propyl-adamantyl-1-acetic acid. The reactivities of substituted derivatives are quite similar to that of the unsubstituted adamantane-1-acetic acid in the esterification reaction of the present invention.

The said higher alcohols having 4 to 20 carbon atoms include straight-chain alkanols such as n-butyl alcohol, n-amyl alcohol, n-hexyl alcohol, n-octyl alcohol, lauryl alcohol, myristyl alcohol and stearyl alcohol; branched-chain alkanols such as i-butyl alcohol, i-amyl alcohol, 2-ethylhexanol-1, 2-methyl-dodecanol-1; straight-chain alkenols such as crotyl alcohol, oleyl alcohol, linoleyl alcohol and the like; branched-chain alkenols such as methallyl alcohol and the like; monocyclic alkanols such as cyclohexanol, methylcyclohexanols, cyclohexyl carbinol; monocyclic unsaturated alcohols such as 2-cyclohexenol; saturated polycyclic alcohols such as 2-decalol, 1-hydroxy-adamantane, 2-exo-hydroxy-exo-trimethylenenorbornane and the like; unsaturated polycyclic alcohols such as 2-exo-hydroxy-2,3-dihydro-exo-dicyclopentadiene, etc.

Although it is usual practice to use either the acid or the alcohol in an amount in excess of the stoichiometric ratio to reduce the reaction time in the esterification reaction of the present invention, use of stoichiometric amounts, of course, leads smoothly to the desired products.

The amount of the catalyst to be used in the present esterification reaction is generally in the range of 0.0001 to 0.1 equivalent, preferably 0.0005 to 0.005 equivalent, per mole of the starting carboxylic acid.

By using a suitable catalyst selected from those described above in the amount indicated, the present esterification reaction can be completed within 24 hours.

The reaction temperature used in the esterification reaction according to the invention is substantially the same as those used in the esterification of ordinary aliphatic carboxylic acids, namely, in the range of 30° to 300° C, preferably 50° to 270° C.

The water produced during the esterification reaction can be removed from the reaction system by any of the known methods such as distillation under reduced pressure, removal by passing an inert gas through the reaction mixture, or use of an azeotropic dehydrating agent. It is preferable in the present process to use an excess of acid rather than an excess of the alcohol if the esters of high boiling point alcohols are to be prepared. Use of excess acid, however, causes the trouble of sublimation of the acid. This is prevented very effectively by the use of an azeotropic dehydration solvent such as n-hexane, cyclohexane, benzene, toluene, xylene and the like.

The present invention is further illustrated by the following examples, where the parts are by weight unless otherwise noted, and all melting points are uncorrected.

EXAMPLE 1

Preparation of butyl ester of adamantane-1-acetic acid (I) (R'=H, R=C_4H_9-)

In a reaction flask equipped with the water separator described in *Organic Syntheses*, Coll. Vol. 3, p. 382, a mixture of 15.45 parts of adamantane-1-acetic acid, 59.30 parts of n-butyl alcohol and 3.74 parts of p-

toluene sulfonic acid crystals was refluxed at 120° to 122° C for 24 hours while separating the water produced during the reaction.

After cooling, the reaction mixture was washed successively with cold water, then with saturated sodium bicarbonate solution (until the washings became distinctly alkaline) and then with cold water, dried over anhydrous potassium carbonate and fractionated under reduced pressure.

The fraction boiling at 98°–100° C (0.06 mm) was collected, giving 14.5 parts (yield 73 percent) of colorless liquid of adamantyl-1-butyl acetate (I), n_D^{22} 1.4867.

ANALYSIS

Found: C, 75.8; H, 10.1; 0, 12.8 percent.

Calculated for $C_{16}H_{26}O_2$: C, 76.75; H, 10.47; O, 12.78 percent.

IR spectrum (liquid film, cm^{-1})

1,735 (*s*): $\nu c = o$, ester

1,260 (*s*), 1,140 (*s*): νc-o-c, ester

NMR spectrum (CCl_4 solution, TMS as internal standard, τ)

6.02 (t, J=7H$_z$, 2H):—COOC$\underline{\underline{H_2}}$—

7.9—8.2 (undissolved resonance)] —(5H): tertiary H's on the adamantane ring and Ad$\underline{\underline{CH_2}}$—

8.3 (s)

8.2—8.5 (undissolved resonance, 12H): secondary H's on the adamantane ring

8.5—8.9 (complex m, 4H): O C$\underline{\underline{H_2}}$($\underline{\underline{CH_2}}$)$_2CH_3$

9.07 (t, J=7H$_z$, 3H):—C$\underline{\underline{H_3}}$

Mass spectrum (*m/e* (relative intensity))

250 (2.2) (parent peak), 195 (9.7), 177 (4.9), 148 (8.2), 135 (100.0)

EXAMPLE 2

Preparation of 2-ethylhexyl ester of adamantane-1-acetic acid (II) (R′=H, R=$CH_3(CH_2)_3CH(C_2H_5)CH_2$-)

Nineteen and four tenths (19.4) parts of adamantane-1-acetic acid, 16.93 parts of 2-ethylhexanol, 0.11 part of zinc oxide and 5.0 parts of xylene were placed in the reaction vessel as described in Example 1, and the mixture was heated to 210° C for 6 hours with stirring while separating the water formed during the reaction.

After cooling to about 50° C, 100 parts by volume of water at 50° C and 100 parts by volume of xylene were added to the reaction mixture, and the resulting mixture was stirred at 50°–60° C for 30 minutes. The xylene layer was separated, washed with cold saturated solution of sodium bicarbonate until the washings became alkaline, followed by washing with cold water until neutral, dried over anhydrous sodium sulfate and than fractionated in vacuo.

The fraction boiling at 133°–135° C (0.09 mm) gave 20.47 parts (yield 68 percent) of (II) as a colorless liquid, n_D^{22} 1.4840.

ANALYSIS

Found: C, 78.2; H, 11.0; O, 10.5 percent.

Calculated for $C_{20}H_{34}O_2$: C, 78.38; H, 11.18; O, 10.44 percent.

IR spectrum (liquid film, cm^{-1})

1,735 (*s*): $\nu c = o$, ester

1,260 (*s*), 1,140(*s*): νc-o-c, ester

NMR spectrum (CCl_4, TMS as internal standard; τ)

6.12 (d, J=7H$_z$, 2H):—COOC$\underline{\underline{H_2}}$—CH

7.8—8.2 (undissolved resonance)] —(5H): tertiary H's on the adamantane ring and Ad$\underline{\underline{CH_2}}$COO—

8.05 (s)

8.2—8.5 (undissolved resonance, 12H): secondary H's on the adamantane ring

8.5—8.95 (undissolved resonance, 9H): CH($\underline{\underline{CH_2}}$)$_3$-, CH$\underline{\underline{H_2}}$-

9.13 (t, J=7H$_z$, 6H): terminal C$\underline{\underline{H_3}}$'s

Mass spectrum (*m/e* (relative intensity))

306 (0.3) (parent peak), 195 (7.9), 193 (6.2), 177 (9.9), 149 (4.8),

148 (6.3), 136 (12.0), 135 (100.0), 133 (8.6)

EXAMPLE 3

Preparation of lauryl ester of adamantane-1-acetic acid (III) (R′=H, R=$C_{12}H_{25}$-)

A reaction mixture comprising 15.54 parts of adamantane-1-acetic acid, 18.63 parts of lauryl alcohol, 0.10 part of stannous oxide and 8.0 parts by volume of xylene was stirred at 210°–220° C for 10 hours in the reaction flask as described in Example 1.

The reaction mixture was diluted with xylene as in the case of Example 2, treated with warm water, and washed with sodium bicarbonate and water, dried over anhydrous sodium bicarbonate and then fractionated in vacuo.

The fraction boiling at 182°–185° C (0.055 mm) was collected to give 21.6 parts (75 percent yield) of (III) as colorless liquid, n_D^{22} 1.4789.

ANALYSIS

Found: C, 79.6; H, 11.0; O, 8.5 percent.

Calculated for $C_{24}H_{42}O_2$: C, 79.50; H, 11.68; O,8.83 percent.

IR spectrum (liquid film, cm^{-1})

1,735 (*s*): $\nu c = o$, ester

1,260 (*m*), 1,135 (*s*): νc-o-c, ester

725 (*w*): ρ-$(CH_2)_n$-, long-chain alkyl (polymethylene).

NMR spectrum (CCl_4 solution, TMS as internal standard, τ)

6.02 (t, J=7H$_z$, 2H):—OC$\underline{\underline{H_2}}$—

7.8—8.2 (uudissolved resonance)] —(5H): tertiary H's on the adamantane ring and Ad$\underline{\underline{CH_2}}$COO—

8.02 (s)

8.2—8.5 (undissolved resonance 12H): secondary H's on the adamantane ring

8.5—8.9 (s, 20H): —OCH$_2$($\underline{\underline{CH_2}}$)$_{10}CH_3$

9 .12 (t, J=7H$_z$, 3H): —C$\underline{\underline{H_3}}$

Mass spectrum (*m/e* (relative intensity))

362 (0.8) (parent peak), 213 (2.0), 195 (27.3), 193 (5.6), 177
(3.2), 168 (1.8), 149 (2.8), 148 (3.5), 136 (11.4), 135 (100.0),
133 (4.4).

EXAMPLE 4

Preparation of stearyl ester of adamantane-1-acetic acid (IV) (R'=H, R=$C_{18}H_{37}$-)

A mixture comprising 15.54 parts of adamantane-1-acetic acid, 27.03 parts of stearyl alcohol, 0.2 parts of stannous oxide and 9.0 parts by volume of xylene was stirred at 210°–230° C for 10 hours in the same apparatus as described in Example 1.

The reaction mixture was treated in the same way as in Example 2. Evaporation of xylene from the dried xylene solution gave a viscous residue which solidified on standing in a refrigerator overnight.

Recrystallization twice from acetone gave 19.9 parts (yield 56 percent) of colorless crystals of pure (IV), m.p. 30.5°–32° C.

ANALYSIS

Found: C, 80.9; H, 12.3; **0**, 6.9 percent.
Calculated for $C_{30}H_{54}O_2$: C, 80.65; H, 12.18; O, 7.19 percent.

IR spectrum (KBr, cm^{-1})
1,735 (*s*): $\nu c = o$, ester
1,260 (*s*), 1,140 (*s*): νc-o-c, ester
725 (*m*): ρ-$(CH_2)_n$-, long-chain alkyl (polymethylene).

NMR spectrum (CCl_4 solution, TMS as internal standard, τ)

6.02 (t, J=7H_z, 2H): $-O\underline{CH_2}-$
7.8–8.2 (undissolved resonance) + 8.02 (s) (5H): tertiary H's on the adamantane ring and $Ad\underline{CH_2}COO-$
8.2–8.5 (undissolved resonance, 12H): secondary H's on the adamantane ring
8.73 (s, 32H): $-OCH_2(\underline{CH_2})_{16}CH_3$
9.11 (t, J= 7H_z, 3H): $-\underline{CH_3}$

Mass spectrum (*m/e* (relative intensity))
446 (1.5) (parent peak), 297 (2.2), 252 (5.2), 195 (38.5),
193 (6.3), 177 (3.0), 149 (2.6), 148 (11.1), 136 (11.1),
135 (100.0).

EXAMPLE 5

Preparation of oleyl ester of adamantane-1-acetate (V) (R'=H, R=$CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_2$-)

A mixture comprising 15.54 parts of adamantane-1-acetic acid, 26.85 parts of oleyl alcohol (purity 78 percent, iodine value 89.1), 0.13 parts of zinc oxide and 9.0 parts of xylene was heated to 190°–196° C with stirring for 8 hours in the apparatus described in Example 1.

The reaction mixture was treated in the same way as in Example 2, and any fractions boiling below 240° (0.065 mm Hg) were distilled off to give 29.2 parts (yield 82 percent) of adamantyl-1-oleyl acetate (V), pale yellow viscous oil, n_D^{21} 1.4670, as the distillation residue.

Saponification value.
Found: 128.2; calculated, 126.2.
Iodine value.
Found: 53.7; calculated, 57.6.
Acid value.
Found: 0.43; calculated, 0.
Hydroxyl value.
Found: 0.76; calculated, 0.

EXAMPLE 6

Preparation of cyclohexyl ester of adamantane-1-acetic acid (VI) (R'=H, R=C_6H_{11}-)

A mixture comprising 15.54 parts of adamantane-1-acetic acid, 80.12 parts of cyclohexanol, and 0.49 part of zinc oxide was stirred at 160°–170° C for 22 hours.

The reaction mixture was allowed to cool down to 50° C, and then diluted with 200 parts by volume of benzene, to which was added 100 parts of warm water at 50° C, and the resulting mixture was stirred for 30 minutes. The organic layer was separated, and washed successively with cold saturated sodium bicarbonate solution and water and dried over anhydrous sodium sulfate.

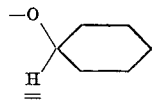
Removal of benzene followed by vacuum fractionation gave 16.65 parts (57 percent yield) of pure (VI), boiling at 142°–143° C (0.08 mm), n_D^{21} 1.5047.

ANALYSIS

Found: C, 77.9; H, 10.2; O, 11.3 percent.
Calculated for $C_{18}H_{28}O_2$: C, 78.21; H, 10.21; O, 11.58 percent.

IR spectrum (liquid film, cm^{-1})
1,730 (*s*): $\nu c = o$, ester
1,260 (*s*), 1,135 (*s*): νc-o-c, ester

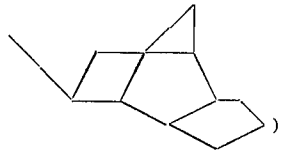
NMR spectrum (CCl_4 solution, TMS as internal standard, τ)

5.1–5.6 (m,1H): 
7.8–8.2 (undissolved resonance) + 8.5 (s): (5H): tertiary H's on the adamantane ring and $Ad\underline{CH_2}COO-$
8.2 – 8.5 (undissolved resonance, 12H): secondary H's on the adamantane ring
8.5 – 9.0 (complex *m*): cyclohexane ring H's

Mass spectrum (*m/e* (relative intensity))
276 (0.7) (parent peak), 195 (77.5), 193 (5.1), 177 (3.8),
149 (2.9), 148 (3.1), 136 (13.9), 135 (100.0), 133 (7.8).

EXAMPLE 7

Preparation of exo-trimethylene-norbornyl-2-exo ester of adamantane-1-acetic acid (VII) (R'=H, R=



A mixture comprising 19.40 parts of adamantane-1-acetic acid, 19.80 parts of 2-exo-hydroxy-exo-trimethylenenorbornane, 0.12 part of zinc oxide, and 10 parts of xylene was stirred at a temperature below 230° for 8 hours.

The reaction mixture was treated in the same way as in Example 2, and the fractionation of the xylene solution gave 21.40 parts (65 percent yield) of pure (VII), boiling at 172°–173° C (0.085 mm), n_D^{22} 1.5250.

ANALYSIS

Found: C, 80.4; H, 9.7; O, 9.6 percent.

Calculated for $C_{22}H_{32}O_2$: C, 80.44; H, 9.83; O, 9.74 percent.

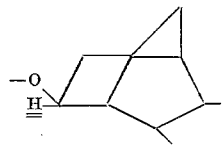
IR spectrum (liquid film, cm^{-1})

1,735 (*s*): $\nu c=o$, ester

1,260 (*s*), 1,140 (*s*): νc-o-c, ester.

NMR spectrum (CCl_4 solution, TMS as internal standard, τ)

4.45 – 4.70 (complex *m*):



7.8 – 9.3 (complex *m*, with peaks at

8.05 (broad S), 8.13 (*s*), 8.43 (broad S)): adamantane

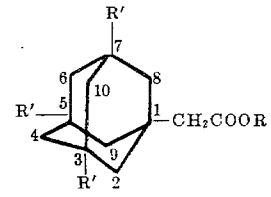
ring H's and trimethylenenorbornane ring H's.

Mass spectrum: (*m/e* (relative intensity))

328 (1.8) (parent peak), 300 (3.0), 195 (2.1), 193 (6.7), 178 (2.0), 177 (14.4), 176 (1.3).

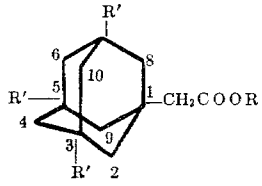
The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A compound of the formula



wherein R is selected from the group consisting of cyclohexyl, methylcyclohexyl, cyclohexenyl, decalyl, adamantyl, exo-trimethylene norbornyl and 2,3-dihydro-exo-dicyclopentadienyl; and R' is H or alkyl having 1 to 4 carbon atoms.

2. A compound of the formula



wherein R is selected from the group consisting of crotyl, oleyl, linoleyl and methallyl; and R' is H or alkyl having 1 to 4 carbon atoms.

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