United States Patent

Gash

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[54] **ESTERS OF TETRAHYDROXY DINEOALKYL ETHERS**

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[52] **U.S. Cl.**.....**260/488 J,** 252/56 S, 252/57, 260/410.5, 260/410.6, 260/468 R, 260/476 R, 260/488 CD

[51] **Int. Cl.**.....**C11c 3/08**

[58] **Field of Search**.....260/410.6, 488 J, 488 CD, 410.5

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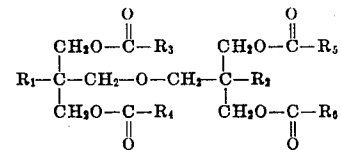
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[57] **ABSTRACT**

Esters of organic monocarboxylic acids and dineoalkyl ethers with a tetrahydroxy functionality and corresponding to the general structure



wherein each R is an alkyl, aryl, or alkyaryl group of one to 12 carbon atoms. These compounds are effective as high performance functional fluids and lubricant base stocks over a wide temperature range.

6 Claims, No Drawings

ESTERS OF TETRAHYDROXY DINEOALKYL ETHERS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to certain new esters of tetrahydroxy dineoalkyl ethers and their uses as lubricants and lubricant base stocks.

2. Description of Prior Art

The continuing development and improvement of high performance aircraft engines has created a continual demand for improved lubricants which are efficient over a wide range of operating temperatures and which are resistant to oxidation and thermal degradation. Jet aircraft engines in particular are found to operate with greater efficiency at higher temperatures, and consequently emphasis for jet engine lubricants has been on the high temperature properties.

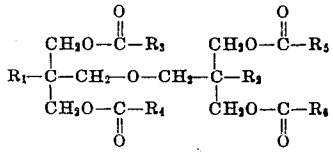
The special requirements of the jet engines led to the development of the synthetic ester lubricants, the first commercial material being di-2-ethylhexyl sebacate. As more severe requirements and particularly higher and higher temperature requirements were placed upon the lubricants, technology advanced and produced the diesters, triesters, and finally polyesters formulated from hindered alcohols.

The hexaesters derived from dipentaerythritol have very good high temperature properties and are widely used as lubricants in modern jet engines. The thermal stability and oxidation resistance of these esters are enhanced through the incorporation of additives such as amines, phenols, phosphites, etc., these additives being well known in the art.

Although emphasis is always directed toward the high temperature properties of the lubricants because these represent the normal operating conditions, it is also important that the lubricant remain fluid at low temperatures in order that the lubricant can flow and perform its function when a cold engine is started. Ideally, the lubricant should have a sufficiently low pour point such that it can be used or stored at temperatures as low as −40° F. The esters of dipentaerythritol are generally deficient in this respect, and require the use of mixed esters and the addition of pour point depresants in order to achieve the desired low temperature fluidity. The use of these additives represents additional cost for raw materials, handling and quality control. Consequently, the discovery of ester compositions which have the good lubricity, thermal stability, and oxidation resistance characteristic of the dipentaerythritol esters, and in addition have superior low temperature properties, would be a major advancement in the state of the high performance lubricant art.

SUMMARY OF THE INVENTION

As a new composition, the esters of this invention are those derived from aliphatic or aromatic mono-carboxylic acids and dineoalkyl ethers having a tetrahydroxy functionality, said esters corresponding to the general structure

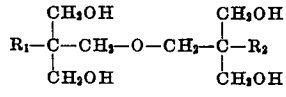


wherein R_1 and R_2 individually are alkyl groups of one to 12 carbon atoms or phenyl, and R_3, R_4, R_5 and R_6 individually are alkyl, aryl, or alkylaryl groups of from one to 12 carbon atoms.

These esters are excellent lubricants and lubricant base materials having exceptional lubricity, thermal stability, and oxidation resistance and having better low temperature properties than the corresponding dipentaerythritol esters.

DESCRIPTION OF PREFERRED EMBODIMENTS

The dineoalkyl ethers used in the preparation of the novel esters of this invention are those compounds which contain four functional hydroxyl groups according to the following structural formula:

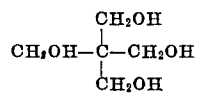


wherein each R is an alkyl group of from one to 12 carbon atoms or phenyl. Typical examples of suitable dineoalkyl ethers where R_1 and R_2 are lower alkyl groups are di-trimethylolethane, di-trimethylolpropane, and trimethylolethane/trimethylolpropane mixed ether. Examples of corresponding ethers where R_1 and R_2 are higher molecular weight alkyl groups or phenyl include di-trimethylol butane, di-trimethylolpentane, di-trimethylolhexane, di-trimethylolheptane, di-trimethyloloctane, di-trimethylolhexane, etc., and mixed trimethylol alkane ethers. An example of the ether where R_1 and R_2 are each phenyl is di-trimethyloltoluene.

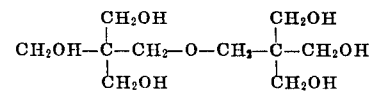
These tetrahydroxy dineoalkyl ethers are conveniently produced by reacting a neoalkoxide ion with a neoalkyl sulfonate to form a cyclic dineoalkyl ether intermediate then hydrolyzing said intermediate to form the tetrahydroxy dineoalkyl ether. In a typical example, a trimethylol alkane is reacted with acetone to form a neoalkyl mono-ol which in turn is reacted with metallic sodium to from a neoalkoxide ion. Additional neoalkyl mono-ol is reacted with toluene sulfonyl chloride to form a neoalkyl tosylate. The tosylate is then reacted with the neoalkoxide ion to form a cyclic dineoalkyl ether intermediate which is subsequently hydrolyzed to form the tetrahydroxy dineoalkyl ether.

The nomenclature used herein corresponds to that commonly employed for di-polyols such as dipentaerythritol (di-PE). Specifically, the compound is named according to the structure on either side of the oxyether linkage, with the oxyether linkage itself being counted as a hydroxyl for each side.

Thus,

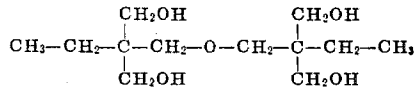


is pentaerythritol, and



is di-pentaerythritol, two hydroxyls being replaced by the oxy-ether linkage.

Accordingly,



is named di-trimethylol propane, even though there are present on the compound only four hydroxyls, two others being replaced by the oxyether linkage.

In order to obtain the novel esters of this invention, a dineoalkyl ether having the tetrahydroxy functionality as defined above is reacted with an aromatic or aliphatic carboxylic acid or mixture of acids, such as acetic, propionic, butyric, valeric, heptanoic, higher aliphatic acids, benzoic and other aromatic acids. The acids may be saturated or unsaturated, although the saturated lower aliphatic acids are generally preferred for ester base lubricants. It is also to be understood that the acid anhydride or other acylating agents may be used as well as the acids themselves.

Illustrative of the novel esters of this invention are: di-trimethylolethane tetra-acetate, -propionate, -butyrate, -valerate, -pelargonate, -benzoate, -neoheptanoate, -cyclopentanecarboxylate, mixed butyrate/benzoate, mixed valerate/isovalerate/decanoate, mixed butyrate/valerate, etc; di-trimethylolpropane tetra-acetate, -butyrate, -valerate, -pelargonate, -benzoate, mixed butyrate/valerate, etc; di-trimethylol-toluene tetra-acetate, -propionate, -butyrate, -valerate, etc; di-(1,1,1-trimethylol-2-ethylhexane) tetra-acetate, -butyrate, -valerate, mixed butyrate/propionate, -benzoate, etc; di-(1,1,1-trimethyloldecane)tetra-acetate, -propionate, -butyrate, -valerate, -benzoate, etc; trimethylol toluene/trimethylolethane ether tetra-acetate, -propionate, -butyrate, -valerate, etc; trimethylol toluene/trimethylolpropane ether tetra-acetate, -propionate, -butyrate, -valerate, mixed acetate/butyrate/valerate, etc; di-trimethylolbutane tetra-acetate, -propionate, -butyrate, -valerate, -cyclopentanecarboxylate, -cyclohexanecarboxylate, mixed butyrate/valerate, etc; ditrimethylol isobutane tetra-acetate, -propionate, -butyrate, -valerate, -mixed benzoate-propionate-valerate, etc.

The novel esters of this invention may be prepared by any of the conventional esterification methods which are well known in the art, the method being not critical to the present invention. For example, the dineoalkyl polyol ethers may be esterified at temperatures between 60° and 180° C., and in the presence of or absence of an inert solvent and esterification catalyst. The crude ester product may be purified by conventional procedures such as washing with alkali to remove excess acid and fractionation to remove volatile impurities.

The dineoalkyl esters of the present invention are useful as lubricants, hydraulic fluids, and other functional fluids for jet engines and in other areas which demand high performance over a wide temperature range. Many of the ester compositions included within the scope of this invention have serviceable viscosities at temperatures ranging from −40° F. to 400° F. or higher. Some of the higher molecular weight compounds are well suited for higher temperature service, such as above 600° F.

The esters of this invention are structurally and chemically related to the dipentaerythritol esters, and may be used as alternative compositions for most of the diPE uses. The esters of this invention are superior to the diPE esters in low temperature viscosity, and are therefore preferred as lubricants and lubricant base stocks for low temperature applications. In this respect, the esters of this invention represent an important advance in the state of the lubrication art.

The following examples are presented to illustrate the invention and to define the properties of some of the novel esters included therein, but are not intended to be limiting of the scope of the present invention.

EXAMPLE I

Preparation of di-trimethylolethane tetracetate

A mixture of 12.3 g. of di-trimethylolethane (di-TME) and 50 ml. of acetic anhydride was heated slowly to 85° C. at which point an exothermic reaction ensued. The solution was refluxed at 130° C. for 10 min., then excess anhydride was removed by distillation. The residue was washed with water, dried, and distilled to obtain 7.9 g. of the desired tetraacetate. b.p. 170°–180° C/0.1—0.15,n D_{25} 1.4,449.

Analysis: Calcd for $C_{18}H_{30}O_9$; C, 55.37; H, 7.75
Found: C, 54.97; H, 7.27

EXAMPLE II

Preparation of di-trimethylolethane tetrabutyrate

A mixture of 47 g. of di-TME and 150 g. of n-butyric anhydride was heated gradually to 160° C. over a 4-hr. period. The excess anhydride was removed by distillation. The residue was washed with water, dried, and distilled to yield 69.1 g. of the desired tetrabutyrate as a colorless oil; b.p. 215°–225° C/0.1 mm., n^{25}_D 1.4,459,

Analysis: Calcd for $C_{26}H_{46}O_9$: C, 62.12; H, 9.23
Found: C, 62.06; H, 9.55

The following table illustrates the superior low temperature properties possessed by the di-TME esters of Examples I and II as compared to the corresponding esters of dipentaerythritol (di-PE).

TABLE I

Compound	MP (°F.)	Density 77°F—40°F		Kinematic Viscosity, cs. 0°F	100°F	210°F	400°F
di-TME tetra-acetate	80.85	1.1122	—	41.700	61.9	5.692	1.137
di-PE hexa-acetate	163	—	—	solid	solid	15.51	1.945
di-TEM tetra-butyrate	(1)	1.0285	14.008	88.42	27.45	4.891	1.199
di-PE hexa-butyrate	84	1.0673	—	solid	69.52	8.947	1.759

(1)Noncrystalline after storage at −40°F. for several weeks.

EXAMPLE III

Preparation of di-trimethylolpropane tetravalerate

A stirred solution of 66.1 millimoles of di-trimethylolpropane, 33.7 g. of valeric acid, 0.3 ml. of 85 percent phosphoric acid and 10 ml. of toluene was

heated at 142° C. for 1½ hours, and finally to 162° C. for 2 hours. Distillation gave the pure tetravalerate, b.p. 218°–216° C/0.1 mm., n^{25}_D 1.4,516.

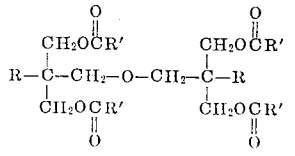
Analysis: Calcd for $C_{32}H_{58}O_9$: C, 65.50; H, 9.96.
Found: C, 65.48; H, 9.78

EXAMPLE IV

A series of esters based upon di-trimethylolethane (di-TME) and di-triemthylolpropane (di-TMP) were prepared from aliphatic and aromatic acids according to the procedure of Example III and evaluated for boiling point, density, and kinematic viscosity. The esters and the analytical results are given in the Table below.

TABLE II

Evaluation of Esters of the Formula



Compound R	R′	Empirical Formula	bp (°F/760 mm)	Density (°F.)	Kinematic Viscosity (°F.) −40	100	210
(1) CH_3	CH_3	$C_{18}H_{30}O_9$	663 (77)	1.1122	—	61.9	5.69
(2) CH_3	C_3H_7	$C_{26}H_{46}O_9$	745 (77)	1.0285	14,008	27.3	4.89
(3) CH_3	C_4H_9	$C_{30}H_{54}O_9$	716 (68)	1.0127	8,334	25.2	4.93
(4) C_2H_5	CH_3	$C_{20}H_{34}O_9$	701 (100)	1.0845	13	86.7	6.90
(5) C_2H_5	C_3H_7	$C_{28}H_{40}O_9$	738 (100)	1.0145	20,966	34.6	5.76
(6) C_2H_5	C_4H_9	$C_{32}H_{58}O_9$	802 (68)	1.0069	11.366	30.7	5.62
(7) CH_3	C_5H_9	$C_{34}H_{54}O_9$	718 (100)	1.0839	—	184	15.4
(8) CH_3	C_7H_{15}	$C_{42}H_{38}O_9$	795 (100)	1.1608	—	180	12.6
(9) CH_3	C_6H_5	$C_{38}H_{38}O_9$	795 (100)	1.1608	—	—	79.4

(1)di-TME tetraacetate
(2) di-TME tetrabutyrate
(3)di-TME tetravalerate
(4)di-TMP tetraacetate
(5)di-TMP tetrabutyrate
(6)di-TMP tetravalerate
(7)di-TME tetracyclopentanoate
(8)di-TME tetraneoheptanoate
(9)di-TME tetrabenzoate

EXAMPLE V

A series of mixed esters based upon di-trimethylolethane and di-trimethylolpropane were prepared by reacting the dineoalkyl ethers with a mixture of carboxylic acids according to the general procedure of Example III. Examples of the mixed esters formed and their physical properties are as follows:

a. di-TME butyrate/benzoate mixed ester
Acid Ratio: butyric/benzoic. . . . 4/1

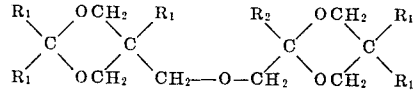
b. di-TME pentanoate/isopentanoate/decanoate mixed ester
Acid Ratio: pentanoic/isopentanonic/decanoic. .40/35/25

c. di-TME butyrate/valerate
Acid Ratio: butyric/valeric. . . . 1/1

d. di-TMP butyrate/valerate
Acid Ratio: butyric/valeric. . . . 1/1

Ester	b.p. °F. 1760 mm	Density (°F.)	Kinematic Viscosity of −40	100	210
a	755	1.0268 (100)	67×10^3	42.1	6.1
b	786	0.9746 (100)	13×10^3	35.3	6.3
c	736	1.0039 (100)	9.9×10^3	26.6	5.0
d	721	1.0054 (100)	18×10^3	34.8	2.1

Although the dineoalkyl esters of this invention are conveniently prepared by esterification of the tetrahydroxy dineoalkyl ethers, this method of preparation is not limiting of the invention. For example, the esters may be formed directly from a precursor of the tetrahydroxy ether which has the following structural formula



wherein each R_1 is an alkyl group of one to eight carbon atoms, and preferably is CH_3, and R_1 and R_2 are individually selected from the group consisting of alkyl groups of one to 12 carbon atoms and phenyl. In this mode of preparation, the cyclic dineoalkyl ether defined above is first hydrolyzed to form the tetrol, then reacted with a selected monocarboxylic acid to form the ester in situ. The step of recovering the tetrol prior to reaction with the acid is thereby eliminated with a resulting savings in processing costs.

This mode of preparation is illustrated by the following example.

EXAMPLE VI

Preparation of di-trimethylolethane tetravalerate

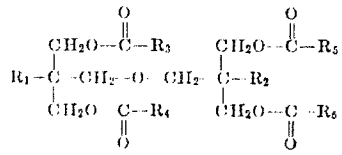
A stirred mixture of 20 g. of di-trimethylolethane bisacetonide, 10 ml. of water and 0.3 ml. of 85 percent phosphoric acid was heated to 62° C. for 5 minutes to obtain a homogeneous solution. Then 33.7 g. of valeric acid was added and the solution was heated to 120° C. allowing overhead distillation of volatiles. Toluene (10 ml.) was added and the solution was refluxed 1½ hours with azeotropic removal of water, then finally heated to 162° C. for 2 hours. Distillation yielded the pure tetravalerate, $n^{25.3}_D$ 1.4,480.

Analysis: Calcd for $C_{30}H_{54}O_9$: C, 64.48; H, 9.74.
Found: C, 64.77; H, 9.58.

The preceeding examples are directed to the esters and mixed esters of the di-TME and di-TMP ethers. However, it is to be understood that these examples are intended simply to illustrate the invention, and the invention is not limited to the demonstrated examples. Other di-trimethylol alkyl and alkaryl ethers as described in this specification can also be employed in accordance with the teachings herein, and therefore the invention is not to be limited except as defined in the appended claims.

What I claim is:

1. An ester represented by the structure



wherein R_1 and R_2 are individually selected from the group consisting of alkyl radicals having from one to 12 carbon atoms and phenyl, and R_3, R_4, R_5 and R_6 are individually alkyl radicals having from one to 12 carbon atoms.

2. An ester of claim 1 wherein R_1 and R_2 are individually selected from the group consisting of CH_3, C_2H_5, and C_3H_7.

3. An ester of claim 1 wherein R_3, R_4, R_5 and R_6 are residues of acids individually selected from the group consisting of acetic, butyric, valeric, pelargonic, and neoheptanoic.

4. An ester of claim 1 selected from the group consisting of

a. di-trimethylolpropane tetraacetate,

b. di-trimethylolpropane tetrabutyrate,

c. di-trimethylolpropane tetravalerate, and

d. di-trimethylolpropane tetraneohepanoate.

5. An ester of claim 1 wherein R_1 and R_2 are CH_3, and R_3, R_4, R_5 and R_6 are alkyl residues of acids individually selected from the group consisting of acetic, butyric, valeric, and neoheptanoic.

6. Di-trimethylolethane tetravalerate.

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