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**FUNAKUBO, EIICHI ET AL: "Introduction of the triphenylmethyl group. V. The mobility of the bromine atom in triphenylmethylisochavibetol and in its derivatives. 2", BERICHTE DER DEUTSCHEN CHEMISCHEN GESELLSCHAFT [ABTEILUNG] B: ABHANDLUNGEN , 71B, 942-7 CODEN: BDCBAD; ISSN: 0365-9488, 1938, XP002712800,**



## DESCRIPTION

[0001] This invention relates to new compounds useful in a method for marking liquid hydrocarbons and other fuels and oils.

[0002] Marking of petroleum hydrocarbons and other fuels and oils with various kinds of chemical markers is well known in the art. A variety of compounds have been used for this purpose, as well as numerous techniques for detection of the markers, e.g., absorption spectroscopy and mass spectrometry. For example, U.S. Pat. No. 7,858,373 discloses the use of a variety of organic compounds for use in marking liquid hydrocarbons and other fuels and oils. However, there is always a need for additional marker compounds for these products. Combinations of markers can be used as digital marking systems, with the ratios of amounts forming a code for the marked product. Additional compounds useful as fuel and lubricant markers would be desirable to maximize the available codes. The problem addressed by this invention is to find additional markers useful for marking liquid hydrocarbons and other fuels and oils.

[0003] Boyd et al, J. Chem. Soc., 1928, pages 630-638, Hardy, J. Chem. Soc., 1929, pages 1000-1011 and Funakubo et al, Berichte der Deutschen Chemischen Gesellschaft, 1938, pages 942-947 disclose tetraphenylmethane derivatives and processes for preparing them. U.S. Pat. No. 5,981,283 discloses a method of tagging liquid hydrocarbon fuels. European patent application 2,441,745 A1 discloses biphenyl ether derivatives that are useful as chemical markers for liquid hydrocarbons and other fuels and oils.

### STATEMENT OF INVENTION

[0004] The present invention provides a compound having formula  $(\text{Ph}_3\text{C})_m\text{Ar}(\text{R}^1)_j(\text{OR}^2)_n$ , wherein Ph represents a phenyl group, Ar is a C<sub>6</sub>-C<sub>12</sub> hydrocarbyl aromatic ring system, R<sup>1</sup> is C<sub>2</sub>-C<sub>12</sub> alkyl or C<sub>4</sub>-C<sub>12</sub> heteroalkyl, R<sup>2</sup> is C<sub>4</sub>-C<sub>18</sub> alkyl or C<sub>4</sub>-C<sub>18</sub> heteroalkyl, m is one or two, j is an integer from one to three and n is an integer from one or two, wherein alkyl is a substituted or unsubstituted hydrocarbyl group having from one to twenty-two carbon atoms in a linear, branched or cyclic arrangement, which is optionally substituted by one or more OH groups, and heteroalkyl is an alkyl group in which one or more methylene groups has been replaced by O or S and it is optionally substituted by OH or C<sub>1</sub>-C<sub>18</sub> alkoxy groups.

[0005] The present invention further provides a method for marking a petroleum hydrocarbon or a liquid biologically derived fuel; said method comprising adding to said petroleum hydrocarbon or liquid biologically derived fuel at least one compound having formula  $(\text{Ph}_3\text{C})_m\text{Ar}(\text{R}^1)_j(\text{OR}^2)_n$ , wherein Ph represents a phenyl group, Ar is an aromatic ring system having from six to twenty carbon atoms, R<sup>1</sup> and R<sup>2</sup> independently are C<sub>1</sub>-C<sub>18</sub> alkyl or C<sub>4</sub>-C<sub>18</sub> heteroalkyl, m is one or two, j is an integer from one to four and n is an integer from one to three; wherein each compound having formula  $(\text{Ph}_3\text{C})_m\text{Ar}(\text{R}^1)_j(\text{OR}^2)_n$  is present at a level from 0.01 ppm to 20 ppm, wherein alkyl is a substituted or unsubstituted hydrocarbyl group having from one to twenty-two carbon atoms in a linear, branched or cyclic arrangement, which is optionally substituted by one or more OH groups, and heteroalkyl is an alkyl group in which one or more methylene groups has been replaced by O or S and it is optionally substituted by OH or C<sub>1</sub>-C<sub>18</sub> alkoxy groups.

### DETAILED DESCRIPTION

[0006] Percentages are weight percentages (wt%) and temperatures are in °C, unless specified otherwise. Concentrations are expressed either in parts per million ("ppm") calculated on a weight/weight basis, or on a weight/volume basis (mg/L); preferably on a weight/volume basis. The term "petroleum hydrocarbon" refers to products having a predominantly hydrocarbon composition, although they may contain minor amounts of oxygen, nitrogen, sulfur or phosphorus; petroleum hydrocarbons include crude oils as well as products derived from petroleum refining processes; they include, for example, crude oil, lubricating oil, hydraulic fluid, brake fluid, gasoline, diesel fuel, kerosene, jet fuel and heating oil. Marker compounds of this invention can be added to a petroleum hydrocarbon or a liquid biologically derived fuel; examples of the latter are biodiesel fuel, ethanol, butanol, ethyl tert-butyl ether or mixtures thereof. A substance is considered a liquid if it is in the liquid state at 20°C. A biodiesel fuel is a biologically derived fuel containing a mixture of fatty acid alkyl esters, especially methyl esters. Biodiesel fuel typically is produced by transesterification of either virgin or recycled vegetable oils, although animal fats may also be used. An ethanol fuel is any fuel

containing ethanol, in pure form, or mixed with petroleum hydrocarbons, e.g., "gasohol." An "alkyl" group is a substituted or unsubstituted hydrocarbonyl group having from one to twenty-two carbon atoms in a linear, branched or cyclic arrangement. Substitution on alkyl groups of one or more OH is permitted. Preferably, alkyl groups are saturated. Preferably, alkyl groups are unsubstituted. Preferably, alkyl groups are linear or branched. An "aryl" group is a substituent derived from an aromatic hydrocarbon compound. An aryl group has a total of from six to twenty ring atoms, unless otherwise specified, and has one or more rings which are separate or fused. Substitution on aryl groups of one or more alkyl or alkoxy groups is permitted. A "heteroalkyl" group is an alkyl group in which one or more methylene groups has been replaced by O or S. Preferably, heteroalkyl groups contain from one to six O or S atoms, preferably from one to four, preferably from one to three. The methylene groups replaced by O or S were bonded to two other carbon atoms in the corresponding alkyl group. Preferably, heteroalkyl groups do not contain S atoms. Preferably, heteroalkyl groups are saturated. Heteroalkyl groups may be substituted by OH or C<sub>1</sub>-C<sub>18</sub> alkoxy groups, preferably OH or C<sub>1</sub>-C<sub>6</sub> alkoxy groups, preferably hydroxy or C<sub>1</sub>-C<sub>4</sub> alkoxy groups. Examples of heteroalkyl groups include oligomers of ethylene oxide, propylene oxide or butylene oxide having two to six units of the alkylene oxide (preferably two to four, preferably two or three) and a terminal hydroxy or C<sub>1</sub>-C<sub>6</sub> alkoxy group (preferably hydroxy or C<sub>1</sub>-C<sub>4</sub> alkoxy, preferably hydroxy or methoxy, preferably hydroxy); an example of an ethylene oxide oligomer is  $-(\text{CH}_2)_2\text{O})_x\text{R}^3$ , where x is an integer from two to six and R<sup>3</sup> is hydrogen or C<sub>1</sub>-C<sub>6</sub> alkyl. Preferably, j is from two to four, preferably two or three. Preferably, R<sup>3</sup> is hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl, preferably hydrogen or methyl, preferably hydrogen. Preferably, the compounds of this invention contain elements in their naturally occurring isotopic proportions.

**[0007]** Ar is an aromatic ring system having from six to twenty carbon atoms and whose substituents include Ph<sub>3</sub>C, R<sup>1</sup> and OR<sup>2</sup> groups, preferably one in which the only substituents are Ph<sub>3</sub>C, R<sup>1</sup> and OR<sup>2</sup> groups. Preferably, Ar is a C<sub>6</sub>-C<sub>12</sub> hydrocarbonyl aromatic ring system. Preferably, Ar is benzene, naphthalene, biphenyl, phenyl ether, diphenylmethane or one of the preceding systems substituted with alkyl and/or alkoxy groups; preferably benzene. Preferably, n is one or two, preferably one. Preferably, m is one. Preferably, j is from one to three, preferably one or two. Preferably, R<sup>1</sup> is C<sub>2</sub>-C<sub>12</sub> alkyl or C<sub>4</sub>-C<sub>12</sub> heteroalkyl, preferably C<sub>2</sub>-C<sub>12</sub> alkyl, preferably C<sub>3</sub>-C<sub>8</sub> alkyl or C<sub>4</sub>-C<sub>8</sub> heteroalkyl, preferably C<sub>2</sub>-C<sub>8</sub> alkyl, preferably C<sub>3</sub>-C<sub>8</sub> alkyl, preferably C<sub>3</sub>-C<sub>6</sub> alkyl, preferably C<sub>2</sub>-C<sub>6</sub> alkyl, preferably C<sub>2</sub>-C<sub>5</sub> alkyl, preferably sec-butyl, t-butyl or isopropyl. Preferably, R<sup>1</sup> is saturated. Preferably, R<sup>1</sup> is linear or branched. Preferably, R<sup>2</sup> is C<sub>2</sub>-C<sub>18</sub> alkyl or C<sub>4</sub>-C<sub>18</sub> heteroalkyl, preferably C<sub>4</sub>-C<sub>18</sub> alkyl or C<sub>4</sub>-C<sub>18</sub> heteroalkyl, preferably C<sub>2</sub>-C<sub>18</sub> alkyl, preferably C<sub>3</sub>-C<sub>18</sub> alkyl or C<sub>4</sub>-C<sub>12</sub> heteroalkyl, preferably C<sub>3</sub>-C<sub>18</sub> alkyl, preferably C<sub>4</sub>-C<sub>18</sub> alkyl, preferably C<sub>6</sub>-C<sub>18</sub> alkyl, preferably C<sub>6</sub>-C<sub>16</sub> alkyl, preferably C<sub>10</sub>-C<sub>14</sub> alkyl. Preferably, R<sup>2</sup> is saturated. Preferably, R<sup>2</sup> is linear or branched, preferably branched.

**[0008]** In using the compounds of this invention as markers, preferably the minimum amount of each compound added to a liquid to be marked is at least 0.01 ppm, preferably at least 0.02 ppm, preferably at least 0.05 ppm, preferably at least 0.1 ppm, preferably at least 0.2 ppm. Preferably, the maximum amount of each marker is 50 ppm, preferably 20 ppm, preferably 15 ppm, preferably 10 ppm, preferably 5 ppm, preferably 2 ppm, preferably 1 ppm, preferably 0.5 ppm. Preferably, the maximum total amount of marker compounds is 100 ppm, preferably 70 ppm, preferably 50 ppm, preferably 30 ppm, preferably 20 ppm, preferably 15 ppm, preferably 12 ppm, preferably 10 ppm, preferably 8 ppm, preferably 6 ppm, preferably 4 ppm, preferably 3 ppm, preferably 2 ppm, preferably 1 ppm. Preferably, a marker compound is not detectable by visual means in the marked petroleum hydrocarbon or liquid biologically derived fuel, i.e., it is not possible to determine by unaided visual observation of color or other characteristics that it contains a marker compound. Preferably, a marker compound is one that does not occur normally in the petroleum hydrocarbon or liquid biologically derived fuel to which it is added, either as a constituent of the petroleum hydrocarbon or liquid biologically derived fuel itself, or as an additive used therein.

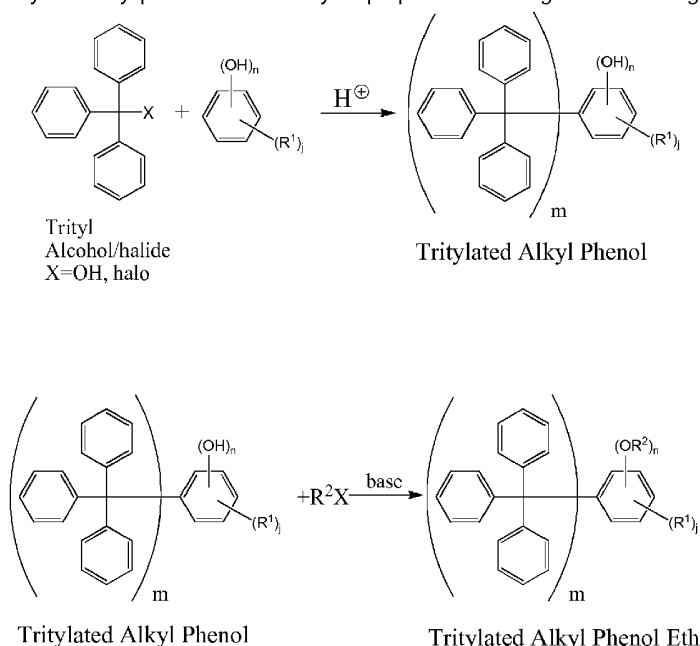
**[0009]** Preferably, the marker compounds have a log P value of at least 3, where P is the 1-octanol/water partition coefficient. Preferably, the marker compounds have a log P of at least 4, preferably at least 5. Log P values which have not been experimentally determined and reported in the literature can be estimated using the method disclosed in Meylan, W.M & Howard, P.H., J. Pharm. Sci., vol. 84, pp. 83-92 (1995). Preferably the petroleum hydrocarbon or liquid biologically derived fuel is a petroleum hydrocarbon, biodiesel fuel or ethanol fuel; preferably a petroleum hydrocarbon or biodiesel fuel; preferably a petroleum hydrocarbon; preferably crude oil, gasoline, diesel fuel, kerosene, jet fuel or heating oil; preferably gasoline.

**[0010]** Preferably, the marker compounds are detected by at least partially separating them from constituents of the petroleum hydrocarbon or liquid biologically derived fuel using a chromatographic technique, e.g., gas chromatography, liquid chromatography, thin-layer chromatography, paper chromatography, adsorption chromatography, affinity chromatography, capillary electrophoresis, ion exchange and molecular exclusion chromatography. Chromatography is followed by at least one of: (i) mass spectral analysis, and (ii) FTIR. Identities of the marker compounds preferably are determined by mass spectral analysis.

Preferably, mass spectral analysis is used to detect the marker compounds in the petroleum hydrocarbon or liquid biologically derived fuel without performing any separation. Alternatively, marker compounds may be concentrated prior to analysis, e.g., by distilling some of the more volatile components of a petroleum hydrocarbon or liquid biologically derived fuel.

**[0011]** Preferably, more than one marker compound is present. Use of multiple marker compounds facilitates incorporation into the petroleum hydrocarbon or liquid biologically derived fuel of coded information that may be used to identify the origin and other characteristics of the petroleum hydrocarbon or liquid biologically derived fuel. The code comprises the identities and relative amounts, e.g., fixed integer ratios, of the marker compounds. One, two, three or more marker compounds may be used to form the code. Marker compounds according to this invention may be combined with markers of other types, e.g., markers detected by absorption spectrometry, including those disclosed in U.S. Pat. No. 6,811,575; U.S. Pat. App. Pub. No. 2004/0250469 and EP App. Pub. No. 1,479,749. Marker compounds are placed in the petroleum hydrocarbon or liquid biologically derived fuel directly, or alternatively, placed in an additives package containing other compounds, e.g., antiwear additives for lubricants, detergents for gasoline, etc., and the additives package is added to the petroleum hydrocarbon or liquid biologically derived fuel.

**[0012]** The compounds of this invention may be prepared by methods known in the art, e.g., alkylation of alkyl phenols or alkyl polyhydroxyaromatics with trityl halide or alcohol, followed by alkylation with organic halides in the presence of base. For example, tritylated alkyl phenolic ethers may be prepared according to the following reaction scheme,



Corresponding compounds in which Ar is not benzene may be prepared from the corresponding substituted aromatic starting materials.

## EXAMPLES

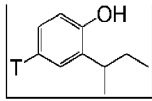
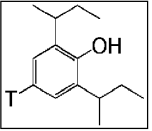
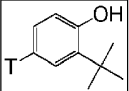
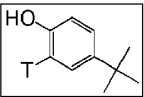
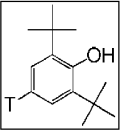
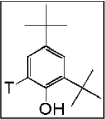
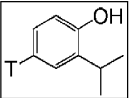
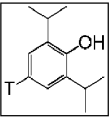
**[0013]** A typical procedure for the synthesis of a trityl alkyl phenol is illustrated by:

2-(sec-Butyl)-4-tritylphenol: A 250 mL 1-neck flask was equipped with a magnetic stirrer and a reflux condenser with nitrogen blanket. The flask was charged with 6.52 grams (0.025 moles) of trityl alcohol, 3.77 grams (0.025 moles) of o-sec-butylphenol, and 50 mL of glacial acetic acid. The mixture was stirred under nitrogen at room temperature to give a clear,

yellow solution. Concentrated sulfuric acid (5 mL) was then added in one portion. The solution immediately became dark red-brown. The solution was stirred at room temperature for 2 days, during which time solids separated out. The reaction mixture was filtered, and the solids were washed on the filter with several portions of water. After drying in a vacuum oven at 65°C for 3 hours, the yield of product was 7.34 grams (75% yield). MP = 135 - 136°C. GPC analysis showed a purity of >99%. The structure was confirmed by IR, <sup>1</sup>H- and <sup>13</sup>C-NMR analyses.

**[0014]** The trityl alkyl phenol compounds prepared by this procedure are listed in Table 1 below.

TABLE 1: Synthesis Data for Trityl Alkyl Phenols

Trityl Phenol (T = triphenylmethyl)	Mol. Wt.	MP, °C	% Yield	[CAS]
	392.53	136 - 136	75	(none)
	448.64	82-91	94	(none)
	392.52	181-182	93	60043-12-1
	392.52	153 - 161	35	97358-11-7
	448.64	157 - 161	89	68869-56-7
	448.64	188 - 200	16	(none)
	378.51	145 - 147	82	(none)
	420.59	142-143	91	(none)

[0015] A typical procedure for the synthesis of a trityl alkyl aryl ether is illustrated by:

((3-(sec-Butyl)-4-(decyloxy)phenyl)methanetriyl)tribenzene (DecTsBuPh): A 500 mL 3-neck flask was equipped with a magnetic stirrer, a reflux condenser with nitrogen blanket, a heating mantle with a temperature controller, and a thermocouple. The flask was charged with 39.32 grams (0.1 mole) of TritosBuPhOH, 6.64 grams (0.1 mole) of 85% potassium hydroxide pellets, and with 250 mL of dimethyl sulfoxide. The mixture was stirred under nitrogen while being heated to 110°C. When all of the potassium hydroxide had dissolved,

the dark colored reaction mixture was cooled to 50°C. Bromodecane (20.7 mL, 22.12 grams, 0.1 mole) was then added in one portion. An exotherm to about 60°C was observed. Heating at 60°C was maintained for 8 hours, then the reaction mixture was poured into about 1200 mL of water containing about 2 grams of potassium hydroxide pellets and about 15 grams of sodium chloride. Toluene (about 300 mL) was added, and the mixture was stirred at room temperature for about 1 hour. The mixture was transferred to a separatory funnel, and the layers were separated. The aqueous layer was washed with 1 x 100 mL of toluene,

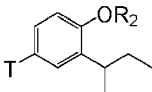
and the washings were combined with the original toluene layer. The toluene solution was dried over anhydrous magnesium sulfate. After filtration, the toluene was removed by rotary evaporation to give 49.48 grams of product as a red oil. Yield was 93%. The structure was confirmed by IR,  $^1\text{H}$ - $^{13}\text{C}$ -NMR, and GC / MS analyses.

**[0016] GC/MS STUDIES:** Stock solutions of each candidate were prepared in dichloromethane (DCM). These solutions were used to establish GC retention times and MS fragmentation patterns, to determine linearity vs. concentration curves from 100 to 1000 ppb, and to demonstrate repeatability and accuracy at 500 ppb concentrations. GC/MS results are shown in Tables 2 and 3.

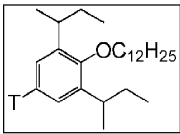
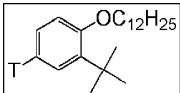
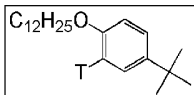
**[0017] GC/MS Parameters:**

- Column: Agilent DB 35m, 15.0 m X 0.25 mm X 0.25  $\mu$
- Flow Rate: 1.5 mL / min. He carrier gas
- Oven: initial: 100°C
- Ramp 1: 20°C / min. to 280°C; Hold: 10 min.
- Ramp 2: 20°C / min. to 340°C; Hold: 6 min.
- Inlet Temp.: 280°C
- Insert: Splitless; Vent: 15 min., Single taper, glass wool, deactivated, 5062-3587
- Injection Volume: 3  $\mu\text{L}$ ; Viscosity: 5 sec., Plunger: fast
- Mass Transfer Line Temp.: 280°C
- MS Quad: 200°C; MS Source: 250°C
- Solvent Delay: 18.5 min.

**TABLE 2: Synthesis Data for Trityl Alkyl o-sec-Butyl Phenol Ethers**

					
R <sub>2</sub>	Mol. Wt.	MP, °C	% Yield	GC Ret Time min.	MS Major Mass, m/e
n-C6 H13	476.69	93-97	81	14.2	476,399
n-C10 H21	532.81	oil	93	20.99	532,455
n-C12 H25	560.85	oil	87	22.25	560,483
n-C14 H29	588.9	oil	88	23.49	588, 511
n-C16 H33	616.96	49-54	82	25.16	616,539

**TABLE 3: Synthesis Data for Trityl Dodecyl Aryl Ethers**

Trityl Dodecyl Aryl Ether (T = triphenylmethyl)	Mol. Wt.	MP, °C	% Yield	GC Ret Time min.	MS Major Mass, m/e
	616.96	oil	79	20.91	616,539,371
	560.85	oil	100	22.32	560,483,315
	560.85	oil	100	19.96	560,377

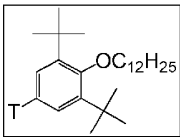
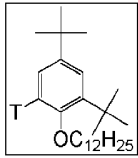
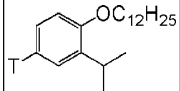
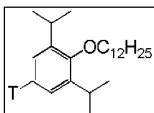
Trityl Dodecyl Aryl Ether				GC Ret Time	MS Major
(T = triphenylmethyl)	Mol. Wt.	MP, °C	% Yield	min.	Mass, m/e
	616.96	oil	75	21.41	616,371
	616.96	114-119	43	616	448,433
	546.84	49-51	91	22.03	546,469,301
	588.9	oil	91	20.64	588, 511, 343

TABLE 4: Stability and Extractability\* Data for DecTsBuPh

	% Change
Standard	0.00
5% NaOH	0.10
50% NaOH	0.60
5% H <sub>2</sub> SO <sub>4</sub>	-0.04
98% H <sub>2</sub> SO <sub>4</sub>	-1.84
2% Charcoal	-0.76
5% Bleach	1.08
Iron Specks	1.76
Fuller's Earth	0.79

\* Test Protocols: 2000 mg/kg solution with internal standard was made in xylenes, then dosed with 5 % by weight of 5% NaOH, 50 % NaOH, 5 % sulfuric acid and 98% sulfuric acid. It was also tested with 2 % charcoal 5 % bleach and 2 % metal specs by wt/wt. The mixtures were stirred gently at room temperature for 8 hours, then the solutions were analyzed by GC and compared to the stock solution.

TABLE 5: Sunlight Stability Data\* for DecTsBuPh

Sunlight	% Change
Standard	0.00
4/5/2012	-1.90
4/13/2012	2.40
4/23/2012	0.90
5/8/2012	-1.40
5/15/2012	1.80

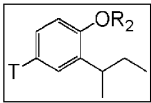
\*The marker sample was made at 2000 mg/.1 concentration with internal standard and checked by GC every week for changes in marker concentration.

[0018] Solubility Studies: Solutions were made from 0.1 grams of marker candidate and 0.9 grams of solvent. The mixtures were



warmed briefly to 60°C to completely dissolve the marker candidate, then the solutions were cooled to room temperature. The solutions were then placed into a -10°C freezer, and the stability of the solutions was monitored for at least 7 days.

**TABLE 6: Solubility Data for Trityl Alkyl o-sec-Butyl Phenol Ethers**

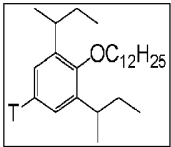
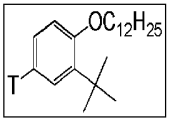
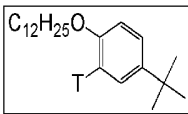
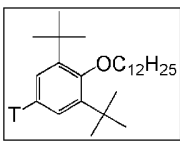
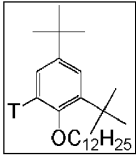
				
R <sub>2</sub>	SOLVENT	SOLUBILITY BEHAVIOR <sup>a</sup>		
		60C	ROOM TEMP	-10C
C <sub>6</sub> H <sub>13</sub>	Aromatic 200	sol	sol	xtls 4D
	DPGDME	sol	sol	xtls 4D
	tetralin	sol	sol	xtls 5D
	NMP	sol	sol	xtls 5D
	DMAc	sol	sol	xtls 4D
	75 : 25 Aromatic			
	150 : cyclohexanone	sol	sol	sol 7D
C <sub>10</sub> H <sub>21</sub>	Aromatic 200	sol	sol	sol 33D
	DPGDME	sol	sol	sol 33D
	tetralin	sol	sol	sol 33D
	NMP	sol	sol	sol 33D
	DMAc	sol	sol	sol 33D
	75 : 25 Aromatic			
	200 : cyclohexanone	sol	sol	sol 33D
	75 : 25 Aromatic			
C <sub>12</sub> H <sub>25</sub>	Aromatic 200	sol	sol	xtls 6D
	DPGDME	sol	sol	sol 70
	tetralin	sol	sol	sol 7D
	NMP	sol	sol	sol 70
	DMAc	sol	sol	sol 70
	75 : 25 Aromatic			
	150 : cyclohexanone	sol	sol	sol 7D
C <sub>14</sub> H <sub>29</sub>	Aromatic 200	sol	sol	sol 7D
	DPGDME	sol	sol	sol 70
	tetralin	sol	sol	sol 70
	NMP	sol	sol	sol 70
	DMAc	sol	sol	xtls 6D
	75 : 25 Aromatic			
	150 : cyclohexanone	sol	sol	sol 7D
C <sub>16</sub> H <sub>33</sub>	Aromatic 200	sol	sol	sol 7D
	DPGDME	sol	sol	sol 70
	tetralin	sol	sol	sol 70

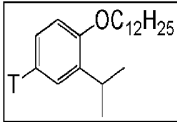
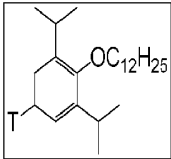
R <sub>2</sub>	SOLVENT	SOLUBILITY BEHAVIOR <sup>a</sup>		
		60C	ROOM TEMP	-10C
	NMP	sol	sol	xtls 6D
	DMAc	sol	sol	xtls 6D
	75 : 25 Aromatic			
	150 : cyclohexanone	sol	sol	sol 7D

a: sol = soluble;  
xtls = crystals  
D = days

[0019] DPGME is dipropylene glycol mono-methyl ether and NMP is N-methylpyrrolidone; AROMATIC 200 and AROMATIC 150 are mixed aromatic solvents available from Exxon Mobil Corp.

**TABLE 7: Solubility Data for Trityl Dodecyl Aryl Ethers**

Trityl Dodecyl Aryl Ether	SOLVENT	60C	SOLUBILITY BEHAVIOR <sup>a</sup> ROOM TEMP	-10C
(T = triphenylmethyl)				
	75 : 25 Aromatic			
	200H : cyclohexanone	sol	sol	sol 7D
	75 : 25 Aromatic			
	200H : o-sec-butylphenol	sol	sol	sol 7D
	75 : 25 Aromatic			
	200H : cyclohexanone	sol	sol	sol 7D
	75 : 25 Aromatic			
	200H : o-sec-butylphenol	sol	sol	sol 7D
	75 : 25 Aromatic			
	200H : cyclohexanone	sol	sol	sol 7D
	75 : 25 Aromatic			
	200H : o-sec-butylphenol	sol	sol	sol 7D
	75 : 25 Aromatic			
	200H : cyclohexanone	sol	sol	sol 7D
	75 : 25 Aromatic			
	200H : o-sec-butylphenol	sol	sol	sol 7D
	75 : 25 Aromatic			
	200H : cyclohexanone	sol	sol	xtls 6D
	75 : 25 Aromatic			
	200H : o-sec-butylphenol	sol	sol	xtls 6D

Trity Dodecyl Aryl Ether	SOLVENT	60C	SOLUBILITY BEHAVIOR <sup>a</sup> ROOM TEMP	-10C
(T = triphenylmethyl)				
	75 : 25 Aromatic			
	200H : cyclohexanone	sol	sol	sol 7D
	75 : 25 Aromatic			
	200H : o-sec-butylphenol	sol	sol	xtls 3D
	75 : 25 Aromatic			
	200H : cyclohexanone	sol	sol	xtls 4D
	75 : 25 Aromatic			
	200H : o-sec-butylphenol	sol	sol	sol 7D
a: sol = soluble; xtls = crystals D = days				

## REFERENCES CITED IN THE DESCRIPTION

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- [US5981283A \[0003\]](#)
- [EP2441745A1 \[0003\]](#)
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- **HARDY**J. Chem. Soc., 1929, 1000-1011 [0003]
- **FUNAKUBO et al.**Berichte der Deutschen Chemischen Gesesellschaft, 1938, 942-947 [0003]
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## PATENTKRAV

1. Forbindelse med formlen  $(\text{Ph}_3\text{C})_m\text{Ar}(\text{R}^1)_j(\text{OR}^2)_n$ , hvor Ph er en phenylgruppe, Ar er et  
aromatisk  $\text{C}_6$ - $\text{C}_{12}$ -hydrocarbylringsystem,  $\text{R}^1$  er  $\text{C}_2$ - $\text{C}_{12}$ -alkyl eller  $\text{C}_4$ - $\text{C}_{12}$ -heteroalkyl,  $\text{R}^2$  er  
5  $\text{C}_4$ - $\text{C}_{18}$ -alkyl eller  $\text{C}_4$ - $\text{C}_{18}$ -heteroalkyl, m er 1 eller 2, j er et helt tal fra 1 til 3, og n er 1 eller  
2,  
hvor alkyl er en substitueret eller usubstitueret hydrocarbylgruppe med fra 1 til  
22 carbonatomer i en lineær, forgrenet eller cyklisk struktur, der eventuelt er substitueret  
med en eller flere OH-grupper, og  
10 heteroalkyl er en alkylgruppe, hvori en eller flere methylen grupper er blevet erstattet med  
O eller S, og den eventuelt er substitueret med OH eller  $\text{C}_1$ - $\text{C}_{18}$ -alkoxygrupper.
2. Forbindelse ifølge krav 1, hvori Ar er et benzenringsystem, j er 1 eller 2, n er 1,  $\text{R}^1$  er  $\text{C}_2$ -  
 $\text{C}_8$ -alkyl,  $\text{R}^2$  er  $\text{C}_4$ - $\text{C}_{18}$ -alkyl, og m er 1.
- 15 3. Fremgangsmåde til mærkning af et petroleumscarbonhydrid eller et flydende biologisk afledt  
brændstof; hvilken fremgangsmåde omfatter tilsætning til petroleumscarbonhydridet eller  
det flydende biologisk afledte brændstof af mindst én forbindelse med formlen  
 $(\text{Ph}_3\text{C})_m\text{Ar}(\text{R}^1)_j(\text{OR}^2)_n$ , hvor Ph er en phenylgruppe, Ar er et aromatisk ringsystem med fra  
20 6 til 20 carbonatomer,  $\text{R}^1$  og  $\text{R}^2$  uafhængigt er  $\text{C}_1$ - $\text{C}_{18}$ -alkyl eller  $\text{C}_4$ - $\text{C}_{18}$ -heteroalkyl, m er 1  
eller 2, j er et helt tal fra 1 til 4, og n er et helt tal fra 1 til 3; hvor hver forbindelse med  
formlen  $(\text{Ph}_3\text{C})_m\text{Ar}(\text{R}^1)_j(\text{OR}^2)_n$  er til stede ved et niveau fra 0,01 ppm til 20 ppm,  
hvor alkyl er en substitueret eller usubstitueret hydrocarbylgruppe med fra 1 til  
22 carbonatomer i en lineær, forgrenet eller cyklisk struktur, der eventuelt er substitueret  
25 med en eller flere OH-grupper, og  
heteroalkyl er en alkylgruppe, hvori en eller flere methylen grupper er blevet erstattet med  
O eller S, og den eventuelt er substitueret med OH eller  $\text{C}_1$ - $\text{C}_{18}$ -alkoxygrupper.
4. Fremgangsmåde ifølge krav 3, hvor Ar er et aromatisk  $\text{C}_6$ - $\text{C}_{12}$ -hydrocarbylringsystem, j er  
30 et helt tal fra 1 til 3, og n er 1 eller 2.
5. Fremgangsmåde ifølge krav 4, hvor  $\text{R}^1$  er  $\text{C}_2$ - $\text{C}_{12}$ -alkyl eller  $\text{C}_4$ - $\text{C}_{12}$ -heteroalkyl.
6. Fremgangsmåde ifølge krav 5, hvor  $\text{R}^2$  er  $\text{C}_4$ - $\text{C}_{18}$ -alkyl eller  $\text{C}_4$ - $\text{C}_{18}$ -heteroalkyl.
- 35 7. Fremgangsmåde ifølge krav 6, hvor Ar er et benzenringsystem, j er 1 eller 2, n er 1,  $\text{R}^1$  er  
 $\text{C}_2$ - $\text{C}_8$ -alkyl,  $\text{R}^2$  er  $\text{C}_4$ - $\text{C}_{18}$ -alkyl, og m er 1.