# Synthesis of Series of Pure Polyethylene Glycol Ethers Based on *n*-Tridecanol, 7-Tridecanol, and Oxo-Process Tridecyl Alcohol

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## Abstract

Pure *n*-tridecyl, 7-tridecyl and *oxo*-tridecyl polyethylene glycol monoethers, $C_{13}H_{27}O(C_2H_4O)_nH$, were made by the Williamson reaction with n = 4,6,8,10 and 12. Related crystalline diethers derived from *n*-tridecanol were made in the range of 4–16 oxyethylene units.

The compounds were extensively purified by crystallization (where applicable) or by chromatography and distillation. The final products are new compounds important for comparative studies of surface properties. Characterizing constants and physical properties including those of a large number of pure intermediates are reported.

All but the lowest member of the *n*-tridecyl monoether series are crystalline, melting between 26 and 40C. The related diethers melting between 37 and 50C have a minimum melting point when they contain between 6 and 8 oxyethylene units. The *oxo*-tridecyl and 7-tridecyl monoethers are liquids.

## Introduction

Ethylene oxide adducts of higher alcohols have become important to the detergent and emulsifier industries. The complexity of such commercial products derives both from the mixture of branched starting alcohols used and from varying amt of ethylene oxide added to each molecule of alcohol. Knowledge of the properties of individual units of such products is clearly valuable in furthering industrial developments, in predicting performance, and in the design of surfactants with specific properties. During basic surface chemical studies of polyoxyethylene alcohols, however, the difficulty of obtaining individual components of known structure in high purity has frequently obstructed the experimental approaches to the problem.

Published research activity in this field has therefore been limited and of very recent date. It is generally concerned with attempts to prepare compounds of known structure bearing similarity to surface active species and with physical measurements on these. Elworthy et al. (7,8) have reported syntheses in a series of hexadecyl monoethers of high mol wt polyglycols during 1962 and 1963 in connection with a study of micellar properties of surfactants. Lange (14,15) and Crook et al. (6) have discussed properties of similar series of compounds but have not given any synthetic details. Several others (3–5,11,12,17,21) have reported related compounds with six or fewer oxyethylene units. Also, Mansfield and Locke (16) have very recently reported the first ten members of a series of polyethylene glycol monoethers of para-(1,1,3,3-tetramethylbutyl)phenol.

Our studies of polyether surfactants were concerned, by contrast, with a differentiation within the fatty alcohol radical, i.e. with three different tridecyl groups: 1) *n*-tridecyl—to obtain data specific to an unbranched alkyl chain, 2) 7-tridecyl—to show the effect of center branching, 3) *oxo*-tridecyl, a commercial mixture of branched-chain groups of the tetramethylnonyl type—to show the effect of complex branching and to relate our studies to commercial products.

These compounds provide an interesting opportunity to study simultaneously the effect of the structure of the lipophilic group and the length of the hydrophilic chain. An initial report of some surface chemical measurements in this series of compounds has appeared in the literature (1) and the publication by Becher of the remaining studies is expected soon. A description of the synthetic work involved and the tabulation of characterizing constants and analyses of the products under study is provided by the present paper. It outlines how each of the isomeric tridecyl alcohols which we chose was reacted in a stepwise fashion to make polyethylene glycol monoethers containing precisely 4,6,8,10 or 12 oxyethylene units.

A summary of the reaction sequences leading to intermediates and the final products is given in Figure 1.

## Experimental

### Preparation of Intermediates

### A. Glycols

*Tri-, tetra-* and *pentaethylene glycols* were isolated from commercial products by fractional distillation and shown to be >99% pure by GLC.

*Hexaethylene glycol* was made from diethylene glycol (Eastman, bp 129–130C/20 mm) and redistilled dichloroethyl ether (bp 72C/16 mm) by Hibbert's (9) method. It was obtained in 48% yield; bp 169–170C/0.12 mm (lit.: 166–168C/0.015 mm), $n_D^{20}$ 1.4644 and hydroxyl number equal 98% of theory.

*Octaethylene glycol* was similarly made from pure triethylene glycol and dichloroethyl ether. Sodium hydride dispersion in mineral oil was used instead of sodium metal to prepare the alcoholate. The product was purified by distillation, preferably after ion exchange. It was obtained in 30% yield; bp 209–220C/0.05 mm (lit.: 206–209C/0.015 mm), $n_D^{20}$ 1.4647 and hydroxyl number equal 102% of theory.

An alternate purification of the glycol via acetylation of the crude product before distillation did not improve the yield. Octaethylene glycol diacetate was obtained in 20% yield; bp 193–209C/0.03 mm, $n_D^{20}$ 1.4562 and saponification equivalent equal 93% of theory.

### B. Tridecanols

*1-Tridecanol* was made by the Grignard procedure of N. Turkiewicz (20) using 1-bromododecane (East-

TABLE I

Preparation of Alkyl Chlorides

| Starting alcohol | Method | $n_D^{20}$ | bp C/mm | Yield % | Chlorine | |
|---|---|---|---|---|---|---|
| | | | | | Calcd. | Found |
| 1-Tridecanol | A | 1.4448 | 103/0.5[a] | 75 | 16.2 | 16.2 |
| Tetraethylene glycol mono-*n*-tridecyl ether | A | 1.4539 | 180–185/0.13 | 49 | 8.98 | 9.67 |
| 7-Tridecyloxyethanol | B | 1.4448 | 110/0.3 | 83 | 13.49 | 13.4[c] |
| Tetraethylene glycol mono-7-tridecyl ether | B | 1.4515 | 160/1 | 62 | 8.98 | 9.0[d] |
| *oxo*-Tridecanol | A | 1.4485 | 64– 69/0.7 | 85 | 15.98[b] | 15.87 |
| Triethylene glycol mono-*oxo*-tridecyl ether | A | 1.4550 | 160–168/0.7 | 60 | 10.02[b] | 10.03 |
| Tetraethylene glycol mono-*oxo*-tridecyl ether | A | 1.4563 | 142–152/0.07 | 68 | 8.91[b] | 9.06 |

[a] Lit. (19): bp 135.7–136°/9 mm.

[b] Eq. wt of *oxo*-tridecanol was 203.5 (based on hydroxyl number determination).

[c] Other Analyses: Calcd.: %C, 68.54; %H, 11.86
Found: %C, 68.72; %H, 12.02

[d] Other Analyses: Calcd.: %C, 63.85; %H, 10.97
Found: %C, 64.34; %H, 12.02

man #896, mp −11 to −9C, refractionated, bp 69–70C/0.03 mm, $n_D^{20}$ 1.4583, 99% pure by GLC) and "Superfyde" paraformaldehyde. The yield of purified product was 78%; bp 106C/0.45 mm, fp 31.5C and >99% pure by GLC. Lit. (20): bp 152C/14 mm, mp 30.5C, yield 60%.

*7-Tridecanol* was made in 70% yield by Grignard reaction from 1-bromohexane (Eastman, refractionated, >99% pure by GLC) and ethyl formate by adaption of the method for di-*n*-butyl carbinol (2). The product melted at 41–43C and was >99% pure by GLC. Lit. (13): mp 41–42C.

*oxo-Tridecyl alcohol* (Enjay Chemical Company, chemical grade) was used as received: hydroxyl number, 276 (calcd. for $C_{13}H_{27}OH$: 280), $n_D^{20}$ 1.4480.

### C. 7-TRIDECYLOXYETHANOL

*Methyl 7-Tridecyloxyacetate.* 7-Tridecanol, dissolved in diglyme, was converted to its sodium salt by the addition of an equivalent of sodium hydride dispersion and heating briefly to 165C. An equivalent of sodium chloroacetate was added in portions at 140C, and the reaction was completed by heating at 165C for one hr. The reaction mixture was poured into dilute $H_2SO_4$ and crude 7-tridecyloxyacetic acid was isolated by extracting with petroleum ether. The acid was methylated in methanol solution with an equivalent of 2,2-dimethoxypropane with $H_2SO_4$ catalyst. The crude ester was isolated by neutralizing with sodium bicarbonate solution, extracting it with petroleum ether, drying and vacuum stripping. It was fractionally distilled twice. Methyl 7-tridecyloxyacetate was obtained in 51% yield; bp 115–118C/0.2 mm, $n_D^{20}$ 1.4387.

Analysis: Calcd. for $C_{16}H_{32}O_3$: %C, 70.52; %H, 11.84. Found: %C, 70.52; %H, 11.90.

*7-Tridecyloxyethanol* was made by reducing methyl 7-tridecyloxyacetate with lithium aluminum hydride (18) in ether at 35C. The product, purified by distillation, was obtained in 94% yield; bp 110–111C/0.2 mm, $n_D^{20}$ 1.4440.

Analysis: Calcd. for $C_{15}H_{32}O_2$: %C, 73.71; %H, 13.20; OH# 229. Found: %C, 73.42; %H, 13.32; OH# 225.

### D. CHLORIDES

Two general methods were used for making the tridecyl chlorides and related compounds. The pyridine method (A) was an adaptation of the procedure recommended by Gerrard (10).

*Method A.* The alcohol was dissolved in a 30% molar excess of pyridine and a 30% excess of thionyl chloride was added at 0–30C (usually 5–15C). If the reaction mixture became excessively thick, more pyridine was added. The chlorosulfinate was decomposed by heating the solution at 100C for three hr. The product was isolated by dissolving the reaction product in benzene (or better, heptane), washing with dilute sodium carbonate and water, and vacuum stripping. Emulsions made the extractions difficult.

*Method B.* The alcohol was added dropwise to a 200% molar excess of thionyl chloride at 0–35C. The formation of the chlorosulfinate was completed at 60–80C for one hr. The excess thionyl chloride was removed and the chlorosulfinate decomposed *in vacuo* (5–10 mm) by gradually raising the temp to 120C until the evolution of sulfur dioxide ceased. The residual alkyl chloride was dissolved in ether and extracted with sodium bicarbonate solution before it was distilled.

The preparation of seven alkyl chlorides by these methods is summarized in Table I.

### E. POLYETHYLENE GLYCOL MONOTRIDECYL ETHERS

*General Method.* These compounds were made by the Williamson synthesis. The alcoholates were formed by reacting metallic sodium (or better, sodium hydride dispersion) under nitrogen with an excess of the glycol (8–20 equivalents) at 27–115C until gas evolution ceased. An equivalent of alkyl chloride was added at 125–145C and the mixture heated at 180–200C for several hr to form the monoether. The reaction mixture was worked up by filtering the salts, vacuum stripping the volatiles and washing the product in chloroform solution with water. Crude yields ranged from 52–89%. The products were further purified by crystallization (where applicable) or by column chromatography on silica gel and distillation.

*Triethylene glycol mono-oxo-tridecyl ether* was made by the General Method using a nine equivalent excess of glycol. The reaction mixture was filtered, diluted with a 1:2 mixture of benzene and heptane, heated briefly, and the lower phase, excess triethylene glycol, discarded. Additional glycol was removed by aqueous extraction. The crude product, obtained in 87% yield upon evaporation, was directly used to make the chloride (above).

## Final Products

### A. MONOETHERS

The 15 polyethylene glycol monotridecyl ethers were prepared by the General Method (above). The crude yields and methods of purification are listed in Table II.

Tables listing the paths of preparation, yield of the purified products, melting points or refractive indices, and analyses are given below.

TABLE II

Purification of the Polyethylene Glycol Monotridecyl Ethers

*n*-Tridecyl ethers

| Glycol units | Crude yield % | Purified by | |
|---|---|---|---|
| 4 | 75[a] | Distillation; bp 191–192C/0.23 mm; $n_D^{20}$ 1.4533. | |
| 6 | 85[a] | Recrystallization from heptane and acetone. | |
| 8 | 89 | Methanol fractional crystallization.<br>Recrystallization from hexane and acetone or silica gel chromatography of mother liquors. | |
| 10 | 66 | Recrystallization from methanol, hexane-acetone, acetone and petroleum ether-benzene. | |
| 12 | 52 | Silica gel chromatography. Recrystallization, twice from acetone. | |
| *oxo*-Tridecyl ethers | | | |
| 3 | 87 | Not further purified prior to conversion to chloride. | |
| 4 | 76 | Two distillations; bp 173–182.5/0.3 mm. | |
| 6 | 75 | DARCO[b] treatment. | |
| 8 | 74 | Silica gel chromatography. DARCO[b] treatment. | |
| 10 | 65 | Silica gel chromatography. DARCO[b] treatment. | |
| 12 | 62 | Silica gel chromatography, twice. | |
| 7-Tridecyl ethers | | | |
| 4[c] | | Alumina chromatography. Molecular distillation at 1 μ. | 140C bath temp |
| 6 | | | 160C bath temp |
| 8 | | | 165C bath temp |
| 10 | | | 180C bath temp |
| 12 | | | 200C bath temp |

[a] Diether also isolated.

[b] Atlas Chemical Industries, Inc. trademark.

[c] Trityl ether; $n_D^{20}$ 1.5245. Analyses: Calcd. for $C_{40}H_{58}O_5$: %C, 77.63; %H, 9.45 Found %C, 77.45; %H, 9.58

### B. DI-*n*-TRIDECYL ETHERS

*Tetraethylene glycol di-n-tridecyl ether* was obtained by filtration of the distillation residue from the monoether synthesis and purified by repeated crystallizations from methanol, mp 39–40C.

*Hexaethylene glycol di-n-tridecyl ether* was obtained on evaporation and partial crystallization of the heptane mother liquors from the hexaethylene glycol monoether preparation. Filtration and recrystallization from methanol yielded the pure diether, mp 36.5–37C.

Data on these and the higher diethers are summarized below. Di-*n*-tridecyl ethers of octaethylene glycol up through hexadecaethylene glycol were prepared according to the General Procedure given below. Somewhat higher yields of the diethers may be expected if a longer reaction time at 200C is used.

*General Procedure.* The reaction was carried out under nitrogen with 15% excess tetraethylene glycol mono-*n*-tridecyl ether monochloride over the selected polyethylene glycol mono-*n*-tridecyl ether in the presence of the calculated amounts of sodium hydride dispersion. The alkoxide was formed at 27–120C, the chloro derivative added at 140–160C and the reactants heated two hr at 200C. The product was purified by taking the reaction mixture up in chloroform, extracting with water, filtering through Super Cel (to remove traces of mineral oil from the sodium hydride dispersion) and then repeatedly recrystallizing it from alcohol.

## Discussion

Our synthetic approach was designed in such a way that difficulties associated with preparing many of the long-chain polyethylene glycols in practical yields and unquestionable purity were largely avoided. We chose to employ glycols up to the octaethylene derivative in our work. Those through pentaethylene glycol were obtained by fractionally distilling commercial products while hexa- and octaethylene glycol were made by Hibbert's method (9). Coupling of shorter fragments of monoethers with the more readily accessible polyethylene glycols to yield final products introduced a measure of flexibility into the overall synthetic sequence. Key intermediates which were used in several subsequent steps and the starting materials (alcohols, chlorides, glycols) were synthesized on a larger scale, i.e. yielding 150–200 g of pure product. The scale of the final preparations was then adjusted to a level which would yield 15–25 g of purified product for study of surface properties.

A. $RCl + H(OC_2H_4)_nOH/NaH = R(OC_2H_4)_nOH$

n—3, 4, 6
R—*n*—$C_{13}H_{27}$
*oxo*—$C_{13}H_{27}$

B. $R(OC_2H_4)_aCl + H(OC_2H_4)_bOH/NaH = R(OC_2H_4)_nOH$

a—1, 3, 4
b—3, 4, 5, 6, 8
n—4, 6, 8, 10, 12
R—*n*—$C_{13}H_{27}$
*oxo*—$C_{13}H_{27}$
7—$C_{13}H_{27}$

C. $R(OC_2H_4)_4Cl + R(OC_2H_4)_nOH/NaH = R(OC_2H_4)_{4+n}OR$

n—4, 6, 8, 10, 12
R—*n*—$C_{13}H_{27}$

D. $ClCH_2COONa + ROH/NaH = ROCH_2COOR'$

R—7—$C_{13}H_{27}$
R'—Na, H, and $CH_3$

$ROCH_2COOCH_3 + LiAlH_4 = ROC_2H_4OH$

FIG. 1. Summary of reaction sequence.

In all syntheses purity rather than yield was emphasized. With the exception of some examples in the preparation of diethers cited under Experimental, however, the yields given in the Tables represent practical values generally to be expected for the specific reactions described. The purity of the final products was insured by using pure starting materials, selecting reactions which give specific products and careful final purification. The volatile intermediates were analyzed by GLC and used only when found to be >99% pure.

*Ethers of n-Tridecanol.* In the *n*-tridecyl series the lower monoethers were made by coupling *n*-tridecyl chloride with tetra- and hexaethylene glycols in the Williamson synthesis (Fig. 1,A). The higher members were made by chain extension. That is, the free hydroxyl of tetraethylene glycol monotridecyl ether was converted into the chloride, and this complex alkyl chloride was used in Williamson syntheses with tetra-, hexa- and octaethylene glycols to make products with 8,10 and 12 units (Figure 1,B). These syntheses were greatly simplified by using sodium hydride dispersion in mineral oil, instead of sodium, to form the alcoholates.

Diethers with 4 and 6 oxyethylene units were obtained in low yield by crystallization from crude preparations of the related monoethers. The higher members of this series were made by coupling monoethers with 4,6,8,10 and 12 oxyethylene units with the monoether monochloride with 4 units (Fig. 1,C). These diethers served as crystalline derivatives to further characterize the monoethers.

Table III summarizes properties, synthetic routes, yields and analyses of the monoethers and diethers based on *n*-tridecanol.

*Ethers of 7-Tridecanol and oxo-Tridecyl Alcohol.* The 7-tridecyl ethers could not be prepared directly by the Williamson reaction because 7-chlorotridecane is readily dehydrochlorinated by alkoxides. However,

TABLE III

Products Based on *n*-Tridecanol

A. Monoethers, R=*n*—$C_{13}H_{27}$
$R(OC_2H_4)_aCl + Na(OC_2H_4)_bOH \rightarrow R(OC_2H_4)_nOH$

| Starting mat'l | | Products | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | Analysis | | | |
| | | | | | Calculated | | Found | |
| EtO units (a) | EtO units (b) | EtO units (n) | Yield % | mp, °C | %C | %H | %C | %H |
| 0 | 4 | 4 | 47 | 25 | 66.98 | 11.78 | 66.93 | 11.81 |
| 0 | 6 | 6 | 50 | 26 –27 | 64.62 | 11.28 | 64.22 | 11.72 |
| 4 | 4 | 8 | 59 | 33 –34 | 63.01 | 10.94 | 63.45 | 11.57 |
| 4 | 6 | 10 | 51 | 37.5–38.5 | 61.84 | 10.70 | 61.95 | 11.51 |
| 4 | 8 | 12 | 35 | 40 –41 | 60.96 | 10.51 | 60.90 | 11.14 |

B. Diethers, R=*n*—$C_{13}H_{27}$
$R(OC_2H_4)_aCl + Na(OC_2H_4)_bOR \rightarrow R(OC_2H_4)_nOR$

| Starting mat'l | | Products | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | Analysis | | | |
| | | | | | Calculated | | Found | |
| EtO units (a) | EtO units (b) | EtO units (n) | Yield % | mp, °C | %C | %H | %C | %H |
| 0 | 4 | 4 | .... | 39 –40 | 73.06 | 12.62 | 73.14 | 13.39 |
| 0 | 6 | 6 | .... | 36.5–37 | 70.54 | 12.15 | 70.18 | 12.76 |
| 4 | 4 | 8 | 19 | 37 –38 | 68.62 | 11.79 | 68.65 | 11.96 |
| 6 | 4 | 10 | 16 | 42.5–43 | 67.11 | 11.51 | 66.98 | 11.78 |
| 8 | 4 | 12 | 25 | 46 –46.5 | 65.90 | 11.28 | 65.73 | 11.24 |
| 10 | 4 | 14 | 23 | 47.5–48 | 64.90 | 11.10 | 64.78 | 11.21 |
| 12 | 4 | 16 | 30 | 49 –49.5 | 65.05 | 10.94 | 63.77 | 11.13 |

TABLE IV

Monoester Products Based on 7-Tridecanol and *Oxo*-Tridecyl Alcohol
$R(OC_2H_4)_aCl + Na(OC_2H_4)_bOH = R(OC_2H_4)_nOH$

A. R = 7-Tridecyl: $(C_6H_{13})_2CH$—

| Starting mat'l | | Products | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | Analysis | | | |
| | | | | | Calculated | | Found | |
| EtO units (a) | EtO units (b) | EtO units (n) | Yield % | $n_D^{20}$ | %C | %H | %C | %H |
| 1 | 3 | 4 | 65 | 1.4508 | 66.98 | 11.78 | 66.87 | 11.56 |
| 1 | 5 | 6 | 70 | 1.4536 | 64.62 | 11.28 | 64.28 | 11.38 |
| 4 | 4 | 8 | 68 | 1.4560 | 63.01 | 10.94 | 62.80 | 11.31 |
| 4 | 6 | 10[a] | 66 | 1.4574 | 61.84 | 10.70 | 61.73 | 10.88 |
| 4 | 8 | 12[b] | 67 | 1.4591 | 60.96 | 10.51 | 60.80 | 10.80 |

B. R = *Oxo*-process tridecyl: Equivalent wt = 186.5

| Starting mat'l | | Products | | | | |
|---|---|---|---|---|---|---|
| | | | | | Analysis—OH number | |
| EtO units (a) | EtO units (b) | EtO units (n) | Yield % | $n_D^{20}$ | Calculated | Found |
| 0 | 4 | 4 | 56 | 1.4556 | 148 | 147 |
| 3 | 3 | 6 | 75 | 1.4590 | 120 | 110 |
| 4 | 4 | 8 | 49 | 1.4602 | 101 | 101 |
| 4 | 6 | 10 | 39 | 1.4615 | 87 | 86 |
| 4 | 8 | 12 | 35 | 1.4635 | 77 | 78 |

[a] For n = 10; mp −15 to −12C.
[b] For n = 12; mp 0 to 4C.

sodium 7-tridecyloxide was condensed with sodium chloroacetate (which cannot be dehydrochlorinated) with good results (13). The alkoxyacetate formed was reduced to the hydroxyethyl derivative of 7-tridecanol (Figure 1,D). The chloride from this alcohol was then condensed with tri- and pentaethylene glycols to give the first two monoethers in the 7-tridecyl series. The higher members of this series were made from the lower members by the methods described for the *n*-tridecyl compounds.

The trityl ether of tetraethylene glycol mono-7-tridecyl ether was prepared and purified by chromatography and molecular distillation. Although it had the proper analysis, it was not crystalline as might be expected from the experience of Gingras and Bayley (12) with similar trityl ethers. No further attempt was made to prepare crystalline derivatives in the 7-tridecyl series.

The *oxo*-tridecyl ethers were made by the methods given for the *n*-tridecyl series. Since the starting alcohol was a mixture of isomers, the products were also complex and the purification was necessarily restricted to homogeneity with respect to length of the hydrophilic chain. By the use of chromatography on silica gel, small amt of diether and residual glycol were removed and fractionation of the isomers resulting from differences in the alkyl group was avoided. Distillations of volatile intermediates were carried out with the same intention and a somewhat wide range in boiling point reflects the presence of isomers within the complex alkyl group.

Table IV summarizes the data obtained in the synthesis of the 7-tridecyl and *oxo*-tridecyl monoethers.

Chlorides were prepared from alcohols either by use of thionyl chloride in pyridine or by use of excess thionyl chloride without other solvent. Yields were similar for both procedures but the latter gave less trouble with emulsions during work-up of oxyethylene derivatives.

The melting points listed in Table III show a minimum in the di-*n*-tridecyl ether series near 6 or 8 oxyethylene units. If the starting alcohol is considered the first member of the mono-*n*-tridecyl ether series (with *n* = 0), a minimum melting point may be observed there also, below four oxyethylene units. Wrigley et al. (21) have observed this phenomenon in their study of monoethers up to four oxyethylene units. They found it to be rather independent of the number of carbon atoms in the alkyl chain, giving examples for compounds derived from dodecyl through hexadecyl radicals. The shift in minimum melting point from a lower oxyethylene number in our monoethers to a higher one in the diethers indicates that the minima are associated with a balance of hydrophilic and lipophilic groups in the molecule. The relative oxyethylene content is thus nearly the same for both monoether and diether at the minima.

The IR spectra of the compounds in all three monoether series are very similar. The *n*-tridecyl and 7-tridecyl series have a weak band reflecting the presence of polymethylene groups. The *oxo*-series has a more complex spectrum as a result of the branched-chain (polymethylated) alkyl group.

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