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Total Synthesis and Structural Verification of Some Novel Branched Alkanes with Quaternary Carbons Isolated from Diverse Geological Sources

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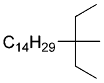

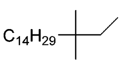

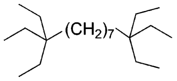

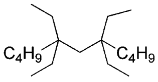

With a view to the authentication of an unusual series of branched alkanes with quaternary centers (BAQCs) isolated from geological samples, and whose structures rest on the interpretation of EI-mass spectral fragmentation patterns, the total synthesis of 3-ethyl-3-methylheptadecane, 3,3-dimethylheptadecane, 3,3,11,11-tetraethyltridecane, and 5,5,7,7-tetraethylundecane is described. The GC-MS data of the first two samples are identical with those of the isolates and confirm their structures. However, the GC-MS data of the two more highly branched structures do not match those of the geological isolates leading to the conclusion that these structures were erroneously assigned.

Total synthesis continues to serve an important role in the verification of structures isolated in minute amounts from natural sources,[1] not infrequently leading to correction of the structures originally proposed.[2] While most natural products isolated in the quest for substances with novel and/or improved therapeutic indexes are obtained from living organisms, geological samples also provide a rich source of novel and unusual structures. Commonly, such geologically derived natural products are isolated in miniscule amounts and their structures rest only on mass spectrometric data, rendering the synthesis of authentic samples of paramount importance. A recent case in point is that of the highly unusual pentacycloanammoxic acid isolated by Sinninghe Damsté from an anaerobic ammonium-oxidizing bacterium,[3] and recently synthesized by the Corey laboratory.[4] The focus of this paper is on an extensive series of branched alkanes containing one or two quaternary carbon atoms, dubbed BAQCs, which were recently tentatively identified in the extractable hydrocarbon fraction of modern and ancient sediments.[5] BAQCs, such as the 5,5-diethylalkanes, were found in geological material ranging in age from modern to 2.1 billion years,[5] and in environments as different as warm (65 °C) deep sea hydrothermal waters, hydrothermal sulfide chimneys, Cretaceous black shales, and modern continental shelf sediments.[5,6] BAQCs have also been recently identified in the total lipid extracts of 26 soil samples collected across China and Mongolia.[7] BAQCs in geological samples are always present as pseudohomologous series with exclusively odd or exclusively even numbers of carbon atoms and are for the vast majority substituted at C-3 or C-5.

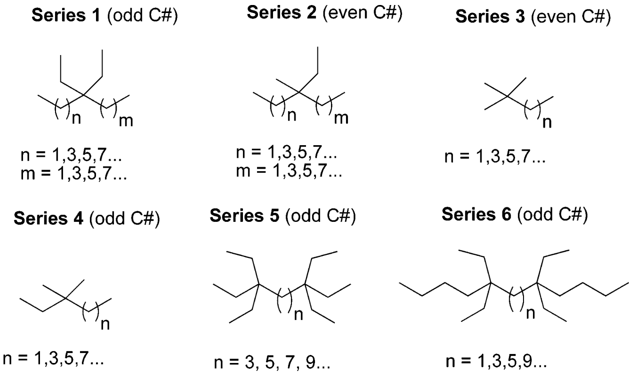

FIGURE 1. Six pseudohomologous series of alkanes with quaternary carbon centers (BAQCs).

Although, BAQCs have a wide distribution in geologic samples, their origin remains unclear as these compounds or their precursors have not been identified in living organisms yet. In geological samples, the hydrocarbon fractions were obtained by Soxhlet extraction of finely powdered sediments followed by extensive column chromatographic separation. The hydrocarbon fraction was finally analyzed by GC-MS, and the structural assignment of BAQCs rests on analysis of the mass spectral fragmentation patterns. The novelty of these branched hydrocarbon structures, coupled with their potential as new geological markers and their unclear biosynthetic pathway, demands the synthesis of authentic samples for purposes of structure verification.

BAQCs are thought to fall into the five main series presented in Figure 1. Previously, we established the validity of Series 1 by the synthesis of two of its members,[5] and we report here on the synthesis and mass spectrometry of representatives of Series 2−6, resulting in the authentication of Series 2−4. On the other hand, the GC-MS data for the synthetic material of representative members of Series 5 and 6 did not match that of the geological isolates, from which we conclude that the structures of these two series must be reassigned.

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(1) For recent work from our own laboratory in this field see: Crich, D.; Dudkin, V. *J. Am. Chem. Soc.* **2002**, *124*, 2263−2266.

(2) Review: Nicolaou, K. C.; Snyder, S. A. *Angew. Chem., Int. Ed.* **2005**, *44*, 1012−1044.

(3) Sinninghe Damsté, J. S.; Rijpstra, W. I. C.; Strous, M.; Jetten, M. S. M.; David, O. R. P.; Geenevasen, J. A. J.; van Maarseveen, J. H. *Chem. Commun.* **2004**, 2590−2591.

(4) (a) Mascitti, V.; Corey, E. J. *J. Am. Chem. Soc.* **2004**, *126*, 15664−15665. (b) Mascitti, V.; Corey, E. J. *J. Am. Chem. Soc.* **2006**, *128*, 3118−3119.

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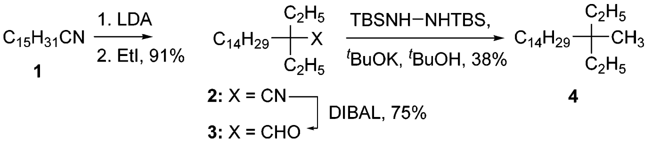
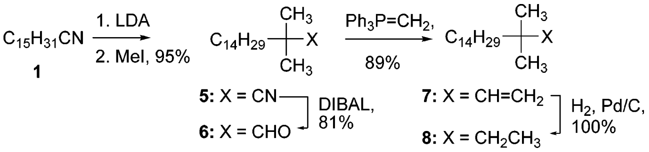
10.1021/jo0603983 CCC: $33.50

SCHEME 1. Synthesis of 3-Ethyl-3-methylheptadecane 4



SCHEME 2. Synthesis of 3,3-Dimethylheptadecane 8



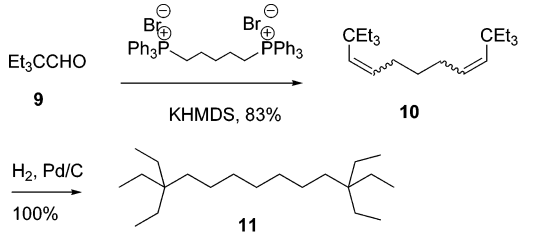
Series 2: Even-Numbered Hydrocarbons with One Ethyl and One Methyl Group on an Odd-Numbered Carbon. Series 2 bears a high resemblance to series 1 from which it differs only by a single methylene group in one of the branches. The synthesis of an authentic sample of a member of this series, 3-ethyl-3-methylheptadecane **4**, began with palmitonitrile (**1**),[8] which was subjected to exhaustive ethylation with lithium diisopropylamide and ethyl iodide to give 2,2-diethylpalmitonitrile **2** in 91% yield. Diisobutylaluminum hydride reduction then afforded the corresponding aldehyde **3**, which was subjected to the Myers modification[9] of the Wolff−Kischner reaction to give the hydrocarbon **4** (Scheme 1).

The perfect match of the EI mass spectrum of **4** with that obtained from the geological isolates and coelution of **4** with the targeted compound (Supporting Information) on two different capillary columns unambiguously confirms the structure of this compound. Taking into account the patterns evident in both the mass spectral fragmentations and gas chromatographic retention times,[6a] it also conveys a high degree of certainty on the other members of this series.

Series 3 and 4: Even-Numbered Hydrocarbons with Two Methyl Groups on an Even-Numbered Carbon and Odd-Numbered Hydrocarbons with Two Methyl Groups on an Odd-Numbered Carbon. These two series bear a very close resemblance differing only by one methylene group at the beginning of the main chain. This resemblance is apparent in the mass spectra with the various peaks in the two series bearing a close similarity, once the offset of 14 m/z units is taken into account.[6a] 3,3-Dimethylheptadecane **8**, a representative member of the two series, was obtained from palmitonitrile by a sequence beginning with exhaustive methylation and reduction to the aldehyde **6** (Scheme 2). Wittig methylenation then afforded the unsaturated hydrocarbon **7**, hydrogenation of which finally provided the target BAQC. Again, the identity of the EI-MS of authentic **8** with that obtained from the original isolates and coelution of **8** with the targeted compound (Supporting Information) on two different capillary columns serves to confirm this structure and to provide very strong support for the two complete series.

Series 5 and 6: Odd-Numbered (m) Hydrocarbons with Four Ethyl Groups either on Carbons 3, 3, ($m - 2$), and ($m - 2$) or on Carbons 5, 5, ($m - 4$), and ($m - 4$). Like Series 3 and 4, Series 5 and 6 bear a close resemblance to each other. Both series were thought to be based on a simple hydrocarbon backbone with an odd-number m of carbons and both have two quaternary carbons each carrying two ethyl groups symmetrically distributed about the center of the main chain. This high degree of similarity in the two series was again manifest in the mass spectral fragmentation patterns.[6a] 3,3,11,11-Tetraethyltridecane was selected as an appropriate example of the two series for synthesis. It was approached by a double Wittig olefination sequence from a commercial bisphosphonium salt and 2,2-diethylbutanal **9**, which provided the diene **10**, predominantly as the *cis,cis*-isomer (Scheme 3). Hydrogenation of this diene then gave the BAQC **11** uneventfully.

SCHEME 3. Synthesis of 3,3,11,11-Tetraethyltridecane 11



The EI mass spectrum of **11** matched that of the targeted compound perfectly (Figure 2). However, in coelution experiments the authentic sample of **11** did not coincide with the targeted compound (Supporting Information), leading to the inevitable conclusion that this compound, and therefore the complete Series 5, was misassigned.[6a]

The invalidation of Series 5 prompted the synthesis of 5,5,7,7-tetraethylundecane **19**, a purported member of Series 6, which distinguishes itself as the only member of the two series with a one-carbon bridge between the two quaternary centers. In contrast to the straightforward assembly of BAQC's **4**, **8**, and **11**, the synthesis of **19** proved considerably more troublesome owing to the close proximity of the two quaternary carbon atoms. Ultimately, a successful unambiguous synthesis was devised beginning from tetramethyl 3,3,5,5-heptanetetracarboxylate **12** (Scheme 4).

Reduction with lithium aluminum hydride afforded the tetraol **13** in 85% yield. Subsequent reaction with benzaldehyde and catalytic p-toluenesulfonic acid in a Dean−Stark apparatus

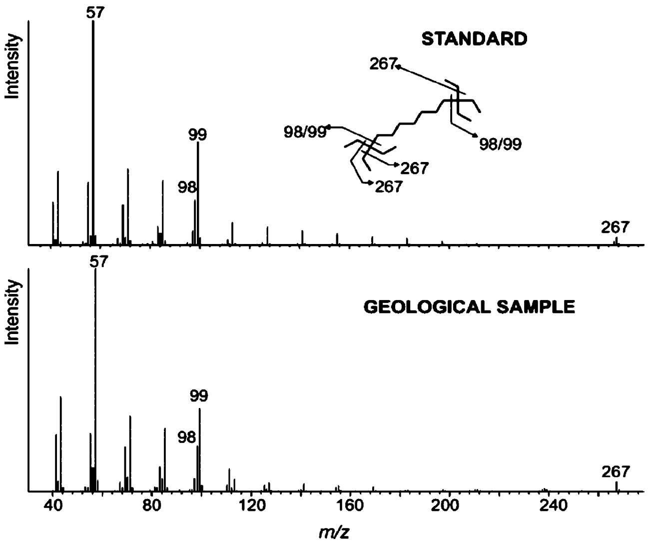


FIGURE 2. EI mass spectra of authentic **11**, and of the targeted geological isolate.

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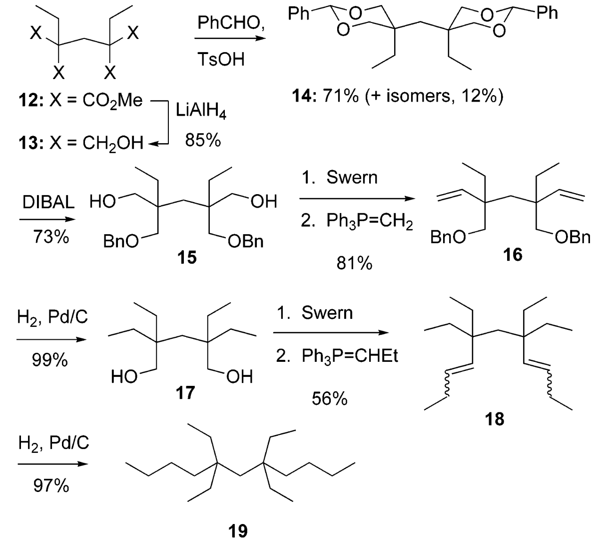
[8] Boivin, J.; El Kaim, L.; Zard, S. Z. *Tetrahedron* **1995**, *51*, 2573−2584.

[9] Furrow, M. E.; Myers, A. G. *J. Am. Chem. Soc.* **2004**, *126*, 5436−5445.

SCHEME 4. Synthesis of 5,5,7,7-Tetraethylundecane 19



provided one major bis(benzylidene) acetal **14**, isolated in 71% yield, together with two minor isomers in 12% yield. On the basis of the symmetry manifest in its NMR spectra, and the equilibrating conditions employed for its synthesis, the major isomer **14** is assigned with two identical benzylidene rings both carrying an equatorial phenyl group. Treatment of the mixture of acetals with DIBAL in dichloromethane then gave the dibenyl ether of the original tetraol in 73% yield, as an unidentified *meso*/*dl* mixture **15**. Swern oxidation then gave the corresponding dialdehyde, which was subjected to Wittig methyleneation to the diene **16**. Hydrogenation over palladium on charcoal brought about reduction of the alkenes and removal of the two benzyl ethers to give the symmetric diol **17**. A second Swern oxidation then afforded a dialdehyde which, with propylidene triphenylphosphorane, gave the diene **18**. Finally, catalytic hydrogenation afforded the BAQC **19** (Scheme 4).

Like **11**, the authentic sample of **19** elutes somewhat differently to the geological isolate leading to the conclusion that this structure and series was also misassigned. In addition, the EI mass spectrum of **19** has several differences from the spectrum recorded for the compound obtained from the geological isolates (Figure 3).[6a] First, the mass spectrum of authentic **19** is dominated by the fragment ion *m*/*z* 127 (100%), corresponding to fragmentation α to the quaternary carbon atom, and formation of a stable tertiary carbocation; the fragment ion *m*/*z* 127 is in much lower relative abundance in the mass spectra of the targeted compound (28%). Second, the fragment ion *m*/*z* 211, which was considered diagnostic of the loss of a butyl substituent in the mass spectra of the targeted geological compound, is not visible in the mass spectrum of authentic **19**. Third, the fragment ion *m*/*z* 239, corresponding to the loss of an ethyl substituent, is in much lower abundance in the mass spectrum of authentic **19** (<1%) than in the mass spectrum of the targeted geological compound (7%). Fourth, the fragment ion *m*/*z* 141, which was thought to correspond to fragmentation β to the quaternary carbon atoms in the mass spectra of the targeted compound, is not present in the mass spectrum of the standard.[10]

In conclusion, the structures of BACQ Series 1−4 are confirmed by the synthesis of authentic samples. Authentic samples of the structures proposed for representative members of Series 5 and 6 had different GC-MS data than those of the geological isolates, leading to the conclusion that these two series have been incorrectly assigned.

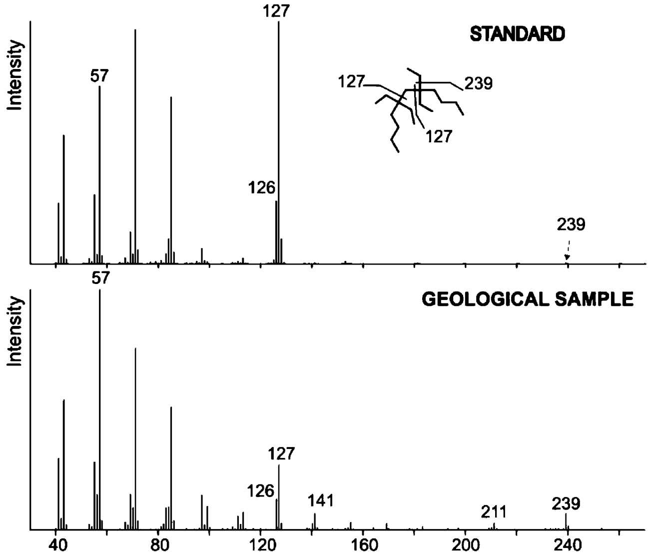


FIGURE 3. EI mass spectra of authentic **19**, and of the targeted geological isolate.

Experimental Section

Bis(5-ethyl-3-phenyl-1,3-dioxan-5-yl)methane (14). A solution of tetraol **13** (1.3 g, 5.9 mmol), benzaldehyde (2.5 g, 23.6 mmol, 4 equiv), TsOH (50 mg), and dry benzene (60 mL) was heated to reflux under a Dean-Stark water separator for 6 h at which point the removal of water was complete. After cooling to rt, Et_3N was added to neutralize the acid before removal of the solvent under vacuum to afford an oily residue, which on silica gel chromatography (eluent: hexane/ethyl acetate 10:1) gave **14** (1.68 g, 71%) and two unseparated minor isomers in a combined yield of 12%. **14**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.93 (t, J = 7.5 Hz, 6H), 1.44 (q, J = 7.5 Hz, 4H), 2.28 (s, 2H), 3.63 (d, J = 11.5 Hz, 4H), 4.11 (d, J = 11.5 Hz, 4H), 5.44 (s, 2H), 7.30−7.40 (m, 6H), 7.45−7.60 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 7.3, 26.7, 29.2, 36.0, 76.4, 102.2, 126.3, 128.3, 128.8, 138.5. Anal. Calcd. for $C_{25}H_{32}O_4$: C, 75.73; H, 8.13. Found: C, 75.74; H, 8.18.

2,4-Bis(benzyloxymethyl)-2,4-diethylpentane-1,5-diol (15). A mixture of **14** and its two isomers (410 mg, 1.03 mmol, 1 equiv) was stirred in dry DCM (10 mL), treated with a solution of DIBALH (2.8 mL, 1.5 M, 4.2 mmol, 4 equiv) in toluene at 0 °C under nitrogen slowly over 15 min, then stirred overnight at rt. Concentrated HCl was added carefully until the solution turned clear. Water (10 mL) and DCM (20 mL) were added to facilitate partitioning. After vigorous stirring for 1 h the aqueous phase was separated and extracted with DCM (3 × 15 mL). The combined organic phases were washed with water (20 mL), saturated aqueous NH_4Cl (20 mL), then brine (20 mL), dried (Na_2SO_4), concentrated under vacuum, and purified by chromatography (eluent: hexane/ethyl acetate 1:1) on silica gel to afford diol **15** (300 mg, 73%) as a colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.70−0.90 (m, 6H), 1.30−1.60 (m, 6H), 2.90−3.20 (br s, 2H), 3.25−3.70 (m, 8H), 4.40−4.60 (m, 4H), 7.20−7.40 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 7.7, 7.9, 26.0, 27.2, 30.6, 31.0, 31.4, 43.2, 43.3, 67.0, 68.0, 73.55, 73.62, 75.3, 76.4, 127.66, 127.74, 127.8, 127.9, 128.46,

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(10) Thus, even if the tentative interpretation of the mass spectrum of the geological compound[6a] was based on a logic fragmentation pattern, as validated for five other BAQCs (three here and two previously[5]), synthesis of an authentic standard is required to avoid over interpretation of the mass spectra of novel isolates from complex mixtures.

128.48, 137.8, 138.1; MS (EI) *m/z* 273, 261, 247, 233, 192, 183, 157, 91. Anal. Calcd for $C_{25}H_{36}O_4$: C, 74.96; H, 9.06. Found: C, 74.90; H, 9.00.

3,5-Bis(benzyloxymethyl)-3,5-diethyl-1,6-heptadiene (16). Oxalyl chloride (0.7 mL, 8 mmol, 4 equiv) was mixed with dry DCM (30 mL) under N_2 and cooled to −78 °C. To this stirred solution was added anhydrous DMSO (1.13 mL, 16 mmol, 8 equiv) slowly over 5 min. After stirring for 20 min, a solution of diol **15** (800 mg, 2 mmol, 1 equiv) in dry DCM (5 mL) was added slowly over 5 min. The mixture was stirred at −78 °C for 1 h before Et_3N (4.5 mL, 32 mmol, 16 equiv) was introduced. The reaction mixture was raised to rt gradually over 2 h, then washed with water (2 × 10 mL) and brine (10 mL), dried (Na_2SO_4), and concentrated under vacuum to afford an oily residue. Purification by chromatography (eluent: hexane/ethyl acetate 20:1 with 1% Et_3N) on silica gel gave the aldehyde (700 mg, 87.5%) as an oil, which was used immediately: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.72 (t, $J = 7.5$ Hz, 6H), 1.50−1.60 (m, 2H), 1.60−1.80 (m, 2H), 1.99 (s, 2H), 3.40 (d, $J = 10$ Hz, 2H), 3.53 (d, $J = 10$ Hz, 2H), 4.21 (d, $J = 11.5$ Hz, 2H), 4.38 (d, $J = 11.5$ Hz, 2H), 7.30 (m, 10H), 9.27 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 7.8, 27.2, 36.3, 53.2, 66.5, 72.7, 127.7, 127.9, 128.4, 137.9, 204.5. A solution of KHMDS (3.8 mL 0.5 M, 1.9 mmol, 3 equiv) in toluene was added slowly to a stirred suspension of methyltriphenylphosphonium bromide (674 mg 1.89 mmol, 3 equiv) in dry THF (15 mL) at −78 °C under N_2 over 5 min. The reaction mixture was raised to rt gradually to give a yellow solution, then cooled to −78 °C, before the above dialdehyde (250 mg, 0.63 mmol, 1 equiv) in dry THF (5 mL) was added. The reaction mixture was stirred overnight, and the resulting solution was filtered through a silica gel pad, washing with 5% ethyl acetate in hexane, and the filtrate was concentrated under vacuum to give a residue. Purification by silica gel chromatography (eluent: hexane/ethyl acetate 20:1) afforded **16** (230 mg, 93%) as an oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ (major, *dl*) 0.69 (t, $J = 7.5$ Hz, 6H), 1.29 (m, 2H), 1.59 (m, 2H), 1.65 (s, 2H), 3.35 (d, $J = 9.0$ Hz, 2H), 3.55 (d, $J = 9.0$ Hz, 2H), 4.40 (d, $J = 12.0$ Hz, 2H), 4.48 (d, $J = 12.0$ Hz, 2H), 4.74 (dd, $J = 18$, 1.5 Hz, 2H), 4.90 (dd, $J = 11$, 1.5 Hz, 2H), 5.78 (dd, $J = 18$, 11 Hz, 2H), 7.20−7.40 (m, 10H); (minor, *meso*) 0.73 (t, $J = 7.5$ Hz, 6H), 1.45 (m, 2H), 1.48 (d, $J = 15$ Hz, 1H), 1.60 (m, 2H), 1.76 (d, $J = 15$ Hz, 1H), 3.31 (d, $J = 9$ Hz, 2H), 3.80 (d, $J = 9$ Hz, 2H), 4.42 (d, $J = 12$ Hz, 2H), 4.46 (d, $J = 12$ Hz, 2H), 4.84 (dd, $J = 18$, 1.5 Hz, 2H), 4.96 (dd, $J = 11$, 1.5 Hz, 2H), 5.79 (dd, $J = 18$, 11 Hz, 2H), 7.20−7.40 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 7.7, 7.9, 29.0, 31.0, 41.2, 43.2, 44.1, 44.2, 71.1, 72.7, 73.0, 73.3, 111.1, 111.9, 127.3, 127.5, 128.2, 139.0, 145.2, 145.3; MS (EI) *m/z* 293, 292, 278, 264, 250, 208,125, 97. Anal. Calcd for $C_{27}H_{36}O_2$: C, 82.61; H, 9.24. Found: C, 82.61; H, 9.26.

2,2,4,4-Tetraethylpentane-1,5-diol (17). Diene **16** (200 mg, 0.51 mmol) was dissolved in ethyl acetate (10 mL), treated with 10% Pd/C (10 mg), and stirred under 1 atm of H_2 overnight. After filtration of the catalyst, the reaction mixture was concentrated to give diol **17** (109 mg, 99%) as an oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.79 (t, $J = 7.5$ Hz, 12H), 1.25 (s, 2H), 1.26−1.40 (m, 8H), 3.1−3.2 (br s, 2H), 3.52 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 7.5, 26.8, 35.9, 41.8, 67.9; MS (EI) *m/z* 186, 185, 169, 155, 154, 151, 139, 111. Anal. Calcd for $C_{13}H_{28}O_2$: C, 72.17; H, 13.04. Found: C, 72.03; H, 12.79.

5,5,7,7-Tetraethylundeca-3,8-diene (18). Diol **17** (260 mg, 1.2 mmol) was converted to the corresponding dialdehyde by Swerm oxidation following the same procedure as for the oxidation of **15**. The crude product was purified by silica gel chromatography (eluent: hexane/ethyl acetate 20:1 with 1% Et_3N) to give the dialdehyde (221 mg yield 87%) as an oil, which was used immediately: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.76 (t, $J = 7.5$ Hz, 12H), 1.36 (q, $J = 7.5$ Hz, 4H), 1.61 (q, $J = 7.5$, 4H), 1.78 (s, 2H), 9.48 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 7.5, 23.8, 28.5, 52.3, 206.3. This dialdehyde (221 mg) was subjected to a Wittig reaction with propylidene triphenylphosphorane following the procedure used in the preparation of **16.** The crude product was purified by silica gel chromatography (eluent: hexane) to afford the diene **18** (180 mg, 65%) as an oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.74 (t, $J = 7.5$ Hz, 12H), 0.96 (t, $J = 7.5$ Hz, 6H), 1.40−1.50 (m, 4H), 1.50−1.60 (m, 6H), 2.10−2.20 (m, 4H), 5.11 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 8.3, 14.7, 22.3, 30.0, 43.9, 45.4, 130.5, 138.1; MS (EI) *m/z* 236, 235, 221, 207, 193, 151, 125, 83. Anal. Calcd for $C_{19}H_{36}$: C, 86.28; H, 13.72. Found: C, 86.30; H, 13.75.

5,5,7,7-Tetraethylundecane (19). Diene **18** (180 mg, 0.68 mmol) was hydrogenated, by the procedure used in the reduction of alkene **10**, to give alkane **19** (178 mg, 97.5%) as an oil: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.77 (t, $J = 7.5$ Hz, 12H), 0.90 (t, $J = 7.0$ Hz, 6H), 1.12 (s, 2H), 1.13−1.21 (m, 4H), 1.21−1.29 (m, 8H), 1.32 (q, $J = 7.5$ Hz, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 8.1, 14.3, 23.8, 25.7, 29.6, 36.7, 37.0, 39.6; MS (EI) *m/z* 239, 127, 126, 117, 96, 86, 71, 57. Anal. Calcd for $C_{19}H_{40}$: C, 84.99; H, 15.01. Found: C, 85.25; H, 15.27.

Mass Spectrometry. Samples were injected at 60 °C onto a HP-5MS capillary column (30 m × 0.25 mm × 0.25 μm). After a 1.5 min hold time, the oven temperature was ramped to 130 °C at 20 deg/min and then to 315 °C at 4 deg/min, using He as carrier gas. The eluent was examined with a mass sensitive detector operating in the EI mode at 70 eV, scanning a mass range of *m/z* 40−650 at 2.44 scans per second.

Coelution Experiments. Samples were injected in the conditions described above for mass spectrometry and were injected as well on a DB-1 capillary column (60 m × 0.25 mm × 1 μm) installed in a HP 5890 gas chromatogram coupled to an FID detector.

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Supporting Information Available: Details of the preparation of **1**−**13**, NMR spectra of all compounds, 70 eV EI mass spectra, and GC data of the synthetic and isolated BAQC's. This material is available free of charge via the Internet at http://pubs.acs.org.

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