A Novel Synthesis of Branched High-molecular-weight (C_{40}^+) Long-chain Alkanes

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Many biological and geochemical questions remain concerning the structures, functions, and properties of naturally occurring high-molecular-weight (C_{40}^+) alkanes with various mid-chain alkylation patterns. Above C_{40}, these alkanes are exceedingly difficult to separate and purify, and syntheses can be blocked by the low solubility of intermediates. To overcome these problems, a facile three-step synthesis employing the alkylation of 1,3-dithiane with a suitable α,ω-dibromoalkane was developed. Bisalkylation of the bis(dithianyl)alkane intermediate with the appropriate 1-bromoalkane and subsequent desulfurization with Raney nickel furnished the desired long-chain alkane. Long-chain alkanes modified at mid-chain and/or symmetrically near the chain termini (or unmodified, i.e., long-chain n-paraffins) are accessible by the selection of appropriate bromoalkanes. Nine mid-chain methylated (C_{38}H_{78} to C_{53}H_{108}), one symmetrical terminal-chain dimethylated (C_{40}H_{82}), and four linear (C_{44}H_{90} to C_{58}H_{118}) long-chain alkanes were synthesized by using this approach. High-temperature gas chromatography (HTGC) was found to have important advantages for evaluating the purity of the synthetic high-molecular-weight alkanes.

Key words: long-chain alkane; linear alkane; branched alkane; dithiane

Long-chain, internally modified (e.g. methylated) alkanes are widely distributed in the natural environment, occurring in extremeophilic bacteria, certain algae, many terrestrial plants and animals, and in geological deposits ranging in age from recent to the Proterozoic period.1–3) The higher-molecular-weight members (containing greater than 40 carbon atoms, i.e., C_{40}^+) of this class of alkanes are important components of the surface waxes of insects and the higher-molecular-weight fractions of petroleum.4–6) Many questions remain concerning the chemical structures, biological functions and physical and chemical properties of these C_{40}^+ long-chain alkanes.

Terrestrial organisms use these higher-molecular-weight alkanes as cuticular waxes to regulate the uptake and loss of water, act as a barrier against microorganisms, prevent the penetration of inorganic chemicals, affect the absorption of agricultural chemicals, and play a role in chemosensory communication.5) Numerous insect classes contain long-chain alkanes with species- or class-specific internal methylation patterns in which certain isomers may act as pheromones or kariomones.5,9)

Long-chain alkanes with internal alkyl modification are components of petroleum microcrystalline waxes and are associated with the organic scale that causes oil-field production problems involving the fouling of wells, pipelines, and petroleum reservoirs.4–6) The carbon number predominance patterns of these higher alkanes can also provide geological information on the source rock paleodepositional environment that is useful in petroleum exploration.4) The importance and diversity of the C_{40}^+ alkanes have become evident with the availability of instrumental techniques such as high-temperature gas chromatography (HTGC).4,6)

The structures of a branched long-chain alkane may not be unequivocally assigned by GC-MS alone.9) Modern methods using meta-stable reaction monitoring or triple quadrapole mass spectrometers aid this assignment, but cannot be applied for alkanes with a carbon number above about C_{40}.9) Moreover, the isolation of individual higher-molecular-weight alkanes from complex mixtures of similar isomers in a biological or geochemical extract may be virtually impossible. Therefore, access to synthetic standards is essential for determining chemical structures and characteristics, and for use in model studies.

A variety of synthetic methods have been employed to prepare long-chain alkanes, including oligomerization of bifunctional starting materi-

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als,9–11) alkylation of β-keto esters,12) extension of carboxylic acids with 1-morpholinocyclooctene,13,14) Blaise ketone synthesis,13) Wurtz coupling12,13,15,16) and the Wittig reaction.17–21) All of these methods can produce only linear long-chain alkanes. Furthermore, in some cases, it is unclear whether the alkane products were pure or contained near-homolog contaminants. Methyl- and dimethyl branched alkanes and related compounds have been synthesized by using several reactions, but the Grignard and related reactions are most frequently employed in the synthesis of branched hydrocarbon chains.22–25) However, most published syntheses report the synthesis of alkanes of moderate chain length (C40).

## Results and Discussion

A procedure has been needed for the rapid preparation of many individual C40 and larger alkanes with various internal alkylation patterns. The procedure has to allow easy separation of the products from by-products and starting materials at each step of the synthesis. Separation and purification of near homologs in this high-molecular-weight range can be exceedingly difficult. The functional group or ‘linker’ used to connect the alkyl chain segments together should improve the solubility of the product in organic solvents. Many alkanes in this molecular weight range have extremely low solubility that can decrease exponentially with increasing carbon number. The linker should also facilitate detection of the desired product and be easily removed in the final step of the synthesis. A fast and accurate analytical method for the characterization of high-molecular-weight alkane products and verification of their purity has also been sought.

In the present study, we report the novel application of the extension of linear or appropriately modified (e.g. methylated) bis(dithianyl)alkanes 1 to the synthesis of long-chain alkanes 2 with a chain length of C40 and larger by using 1,3-dithiane as a linker group. A significant advantage of this approach is that three alkane fragments of moderate chain length (and reasonable solubility) are assembled in the final synthetic step to form the desired long-chain alkane of significantly low solubility. As shown in Scheme 1,

![Scheme 1. Synthesis of Linear and Branched Long-chain Alkanes 2.](image-url)
Synthesis of Branched Long-chain Alkanes

Table 1. Synthesis of Bis(dithianyl)alkanes

<table>
<thead>
<tr>
<th>Product</th>
<th>Temperature (lithiation) [°C]</th>
<th>Temperature (alkylation) [°C]</th>
<th>Yield [%]</th>
<th>Mp [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>−45</td>
<td>−30</td>
<td>61</td>
<td>85</td>
</tr>
<tr>
<td>1b</td>
<td>−45</td>
<td>−30</td>
<td>78−79</td>
<td>85</td>
</tr>
<tr>
<td>1c</td>
<td>−10</td>
<td>−30</td>
<td>41</td>
<td>98−99</td>
</tr>
<tr>
<td>1d</td>
<td>−10</td>
<td>−10</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>1e</td>
<td>−10</td>
<td>−4</td>
<td>18−32</td>
<td>74</td>
</tr>
<tr>
<td>1f</td>
<td>−15</td>
<td>−15</td>
<td>57</td>
<td>oil</td>
</tr>
<tr>
<td>1g</td>
<td>−15</td>
<td>−15</td>
<td>37−54</td>
<td>oil</td>
</tr>
<tr>
<td>1h</td>
<td>−15</td>
<td>−15</td>
<td>48</td>
<td>oil</td>
</tr>
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Table 2. Bisalkylation of Bis(dithianyl)alkanes

<table>
<thead>
<tr>
<th>Dithiane (1)</th>
<th>1-Bromoalkane (5)</th>
<th>Temperature [°C] Lithiation</th>
<th>Temperature [°C] Alklyation</th>
<th>Monoalkylated (7) Yield [%]</th>
<th>Mp [°C]</th>
<th>Bisalkylated (6) Yield [%]</th>
<th>Mp [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>5f</td>
<td>−10</td>
<td>−10</td>
<td>7a</td>
<td>70</td>
<td>6a</td>
<td>50−67</td>
</tr>
<tr>
<td>1b</td>
<td>5f</td>
<td>−20</td>
<td>−10</td>
<td>7d</td>
<td>37−38</td>
<td>6d</td>
<td>67</td>
</tr>
<tr>
<td>1c</td>
<td>5f</td>
<td>23</td>
<td>−10</td>
<td>7e</td>
<td>31−32</td>
<td>6e</td>
<td>36</td>
</tr>
<tr>
<td>1e</td>
<td>5b</td>
<td>−15</td>
<td>−15</td>
<td>7g</td>
<td>10</td>
<td>6g</td>
<td>47</td>
</tr>
<tr>
<td>1f</td>
<td>5d</td>
<td>−15</td>
<td>−15</td>
<td>7h</td>
<td>11</td>
<td>6h</td>
<td>66</td>
</tr>
<tr>
<td>1g</td>
<td>5e</td>
<td>−15</td>
<td>−15</td>
<td>7i</td>
<td>(13)nc</td>
<td>6i</td>
<td>62</td>
</tr>
<tr>
<td>1h</td>
<td>5f</td>
<td>−15</td>
<td>−15</td>
<td>7j</td>
<td>12</td>
<td>6j</td>
<td>45</td>
</tr>
<tr>
<td>1i</td>
<td>5c</td>
<td>−15</td>
<td>−15</td>
<td>7k</td>
<td>—</td>
<td>6k</td>
<td>71</td>
</tr>
<tr>
<td>1j</td>
<td>5e</td>
<td>−15</td>
<td>−15</td>
<td>7l</td>
<td>—</td>
<td>6l</td>
<td>55</td>
</tr>
<tr>
<td>1k</td>
<td>5d</td>
<td>−15</td>
<td>−15</td>
<td>7m</td>
<td>—</td>
<td>6m</td>
<td>16</td>
</tr>
<tr>
<td>1l</td>
<td>5e</td>
<td>−15</td>
<td>−15</td>
<td>7n</td>
<td>—</td>
<td>6n</td>
<td>77</td>
</tr>
</tbody>
</table>

a 1-Bromoalkane 5 = 3.0 equivalents; n-BuLi = 3.0 equivalents.  b 1-Bromoalkane 5 = 3.2 equivalents; n-BuLi = 3.2 equivalents.  c 1-Bromoalkane 5 = 3.0 equivalents; n-BuLi = 3.2 equivalents.  d 1-Bromoalkane 5 = 3.0 equivalents; n-BuLi = 4.0 equivalents.  e The compound was not fully characterized.

the first step in our approach was the alkylation of 1,3-dithiane with suitable dibromoalkane 4. Bisalkylation of resulting bis(dithianyl)alkane 1 with 1-bromoalkane 5 furnished desired long-chain compounds 6 as well as small amounts of monoalkylated compounds 7. Alkanes 2 were obtained in the third step after hydrogenolysis with Raney nickel in cyclohexane.27,28

Synthesis of bis(dithianyl)alkanes 1

Bisdithianes 1 were obtained by alkylation 1,3-dithiane (3) with dibromides 4 (see the table in Scheme 1) in THF (Table 1). The yield of the alkylation reaction was highly temperature dependent, the optimal temperature range for the alkylation of 4a-c and 4e-h being −15°C to −10°C. Linear α,ω-dibromoalkanes 4a-c are insoluble in THF at a temperature below −30°C. Linear dibromides with a chain length of more than 18 carbon atoms are even less soluble in THF and, therefore, cannot be employed in this approach. Overall, the reaction of 1,3-dithiane (3) with 4a-c and 4e-h proceeded smoothly in a moderate to good yield (Table 1).

Dibromides with an adjacent branching point, for example 4d, were found to be less suitable for this approach. No reaction of 2-lithio-1,3-dithiane was apparent with branched α,ω-dibromoalkane 4d at −10°C, although 1d was obtained in a yield of only 18−32% at 4°C. The low reactivity of 4d toward the nucleophile (i.e. the anion of 3) is probably ascribable to steric hindrance due to the methyl substituent adjacent to the reaction site, which might have caused the elimination of HBr under the basic reaction conditions employed.

Bisalkylation of bis(dithianyl)alkanes 1

Bis(dithianyl)alkanes 1a-c as well as higher 1-bromoalkanes such as 5f are insoluble in THF at a temperature below −30 to −25°C. In our experience, the solubility of these compounds decreases dramatically with increasing chain length. As a result, the lithiation of 1c requires a much higher temperature (23°C) than does the lithiation of 1a and 1b (≤ −10°C) (Table 2). However, performing the alkylation reaction at a higher temperature reduces the yield of the alkylation products. Yellow products were observed whenever the alkylation reaction was performed at an elevated temperature, indicating decomposition of the starting materials and/or products. This solubility problem might be circumvented by using a different solvent, but unfortunately, bis(dithianyl)alkanes 1a-c are even less soluble in solvents such as ether and DME. Overall, our observations suggest that the chain length of the linear cen-
Bisalkylation of 1d with 1-bromodocosane (5f) was unsuccessful, only 50% of the starting material (1d) being recovered at −15 °C due to decomposition. However, at 4 °C, we were able to isolate 34–36% of the monoalkylated product. A small fraction (12%) of an impure dialkylated product was also isolated, but we were unable to further purify and characterize this fraction. After desulfurizing the impure fraction, an HTGC analysis showed a single major product that seemed to be a branched alkane, thus providing evidence that this fraction indeed contained the desired bisalkylated product.

Consequently, 1,3-dibromo-2-methylpropane (4d) was not a suitable starting material for the synthesis of methyl branched alkanes. Not only was the synthesis of corresponding bis(dithianyl)alkanes 1d difficult, but the bisalkylation of 1d did not proceed readily or in a good yield. In contrast to linear bis(dithianyl)alkanes 1a–c, 1d has a branching point (tertiary carbon) near the dithiane moieties. It was thus believed possible to obtain a higher yield of desired bisalkylated products 6 by moving the branching point, e.g. the methyl group, further away from the dithiane moieties. Based on this hypothesis, we synthesized methyl branched bis(dithianyl) alkanes 1e–h and studied their alkylation. The bisalkylation of 1e–h in the presence of 4 equivalents of butyllithium and 3 equivalents of 1-bromoalkane 5 indeed yielded desired bisalkylated products 6 in a good yield (45–77%), Table 2).

Alkanes with more than one methyl group are constituents of the cuticular hydrocarbons of many insects. The symmetrical dimethylalkane, 13,23-dimethylpentatriacontane, is a sex pheromone of the tsetse fly (Glossina pallidipes). We investigated the possibility of using our approach to synthesize long-chain dimethylalkanes of this type, and were able to synthesize 9,30-dimethyloctatriacontane 8 by the bisalkylation of 1b with 1-bromo-4-methyldodecane 9 and subsequent desulfurization (Scheme 2). Branched 1-bromoalkane 9 was synthesized from cictronellol by following the procedure of Mori and co-workers, the only deviation from their synthetic approach being the direct transformation of 2,6-dimethyltetradec-2-ene to 4-methylundecanol by reductive ozonolysis with O3 and NaBH4.

**Scheme 2.** Synthesis of 9,30-Dimethyloctatriacontane 8, a Symmetrical Dimethyl Alkane.

**Table 3.** Monoalkylation of Bis(dithianyl)alkanes 1

<table>
<thead>
<tr>
<th>Dithiane (1)</th>
<th>1-Bromoalkane (5)</th>
<th>n-BuLia eq.</th>
<th>Monoalkylated (7) Yield [%]</th>
<th>Bisalkylated (6) Yield [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>b</td>
<td>5a</td>
<td>0.7</td>
<td>7b 33</td>
<td>6c 16</td>
</tr>
<tr>
<td>b</td>
<td>5b</td>
<td>3.0</td>
<td>7c 50</td>
<td>6c 22</td>
</tr>
<tr>
<td>b</td>
<td>5b</td>
<td>1.0</td>
<td>7c 39</td>
<td>6c 33</td>
</tr>
<tr>
<td>b</td>
<td>5b</td>
<td>1.3</td>
<td>7c 34</td>
<td>6c 40</td>
</tr>
<tr>
<td>e</td>
<td>5a</td>
<td>1.0</td>
<td>7f 47</td>
<td>6f 16</td>
</tr>
</tbody>
</table>

* Lithiation temperature = −10 °C except for 1e at −15 °C. Alkylation temperature = −10 °C except for 1e at −15 °C.

b 6f: mp = 39–40 °C
Synthesis of Branched Long-chain Alkanes

Table 4. Synthesis of Linear and Branched Long-chain Alkanes 2

<table>
<thead>
<tr>
<th>Product/Name</th>
<th>Formula</th>
<th>Yield[^a] [%]</th>
<th>Purity[^a]</th>
<th>Mp [°C]</th>
<th>Mp (lit.) [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>Hexapentacontane</td>
<td>C_{64}H_{114}</td>
<td>61</td>
<td>95.1</td>
<td>97.1</td>
</tr>
<tr>
<td>2b</td>
<td>Tetratetracontane</td>
<td>C_{32}H_{66}</td>
<td>79</td>
<td>99.9</td>
<td>88.5[^c]</td>
</tr>
<tr>
<td>2c</td>
<td>Hexatetracontane</td>
<td>C_{40}H_{82}</td>
<td>79</td>
<td>99.9</td>
<td>88.5[^c]</td>
</tr>
<tr>
<td>2d</td>
<td>Octapentacontane</td>
<td>C_{56}H_{106}</td>
<td>38(78)[^d]</td>
<td>98.5</td>
<td>98.8</td>
</tr>
<tr>
<td>2e</td>
<td>19-Methylheptatriacontane</td>
<td>C_{54}H_{108}</td>
<td>86</td>
<td>87.4</td>
<td>42-45</td>
</tr>
<tr>
<td>2f</td>
<td>20-Methylnonatetracontane</td>
<td>C_{58}H_{118}</td>
<td>71</td>
<td>97.4</td>
<td>47</td>
</tr>
<tr>
<td>2g</td>
<td>22-Methyltritriacontane</td>
<td>C_{56}H_{112}</td>
<td>74</td>
<td>88.3</td>
<td>50-53</td>
</tr>
<tr>
<td>2h</td>
<td>23-Methylpentatetracontane</td>
<td>C_{58}H_{118}</td>
<td>82</td>
<td>92.6</td>
<td>54-57</td>
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<tr>
<td>2i</td>
<td>26-Methylpentacontane</td>
<td>C_{54}H_{108}</td>
<td>82</td>
<td>n.d.</td>
<td>58-59</td>
</tr>
<tr>
<td>2j</td>
<td>21-Methylhexadecatetracontane</td>
<td>C_{64}H_{128}</td>
<td>65</td>
<td>74.0</td>
<td>46-49</td>
</tr>
<tr>
<td>2k</td>
<td>21-Methylheptadecatetracontane</td>
<td>C_{66}H_{132}</td>
<td>67</td>
<td>81.9</td>
<td>48-50</td>
</tr>
<tr>
<td>2l</td>
<td>22-Methylheptatriacontane</td>
<td>C_{62}H_{118}</td>
<td>71</td>
<td>83.2</td>
<td>48-51</td>
</tr>
<tr>
<td>2m</td>
<td>21-Methylheptadecatetracontane</td>
<td>C_{66}H_{132}</td>
<td>72</td>
<td>81.8</td>
<td>48-51</td>
</tr>
<tr>
<td>2n</td>
<td>21-Methylpentatetracontane</td>
<td>C_{58}H_{112}</td>
<td>65</td>
<td>98[^e]</td>
<td>47-49</td>
</tr>
</tbody>
</table>

[^a]: Values in parentheses are crude yields.[^b]: Purity determined from HTGC peak areas in the C15 to C90 range.[^c]: A solid state transition was observed at 74.5°C.[^d]: A solid state transition was observed at 74.5°C.[^e]: Additional 28% of impure 2d was obtained from the filtrate, mp = 91°C.[^f]: Purity based on C15 to C90 peak intensities.

Sequential alkylation of bis(dithianyl)alkanes 1

Many branched alkanes could be made available by dividing the alkylation of bis(dithianyl)alkanes 1 into two separate steps. We first optimized the monoalkylation of bis(dithianyl)alkanes 1, a good yield of monoalkylated compounds 7 (50%) being obtained by using an approximately threefold excess of butyllithium (Table 3). To our surprise, the second alkylation step proved to be extremely difficult, because monoalkylated bis(dithianyl)alkanes 7 that were studied (see Table 3) seemed to be susceptible to degradation in the presence of butyllithium.

Desulfurization

Different synthetic methods, including Raney nickel and nickel boride, have been reported for the desulfurization of organic compounds.

Methods for the desulfurization of sulfur-rich geomacromolecules are of particular interest for our synthetic approach because of the structural similarity (long hydrocarbon chains) of these compounds to bis-alkylated bis(dithianyl)alkanes 6. Several desulfurization methods have been developed for these ubiquitous organic sulfur compounds because they are potentially valuable paleo-environmental indicators. Raney nickel in ethanol is probably the most commonly employed reagent, but nickel boride is also a suitable desulfurization agent. Gensler and co-workers have described the use of Raney nickel in cyclohexane for a synthesis of DL-methyl meromycolate, and Mori and co-workers have employed Raney nickel in dioxane for the synthesis of 13,23-dimethylpenta-triacontane. Based on this literature assessment, we studied the desulfurization of 6a with Raney nickel in ethanol, dioxane/water and cyclohexane. We also performed some preliminary experiments with nickel boride. Only cyclohexane as a solvent gave the desired alkanes 2 in a satisfactory yield and purity, and, consequently, all desulfurization experiments were performed with freshly prepared Raney nickel in cyclohexane (Table 4).

The principal difficulty encountered in the final step of the synthesis of linear alkanes was again the solubility of the starting materials and the products. A large excess of Raney nickel and the use of cyclohexane as the solvent did not result in a pure product, although no sulfur was present in the product as shown by a combustion analysis. However, repetition of the desulfurization reaction furnished the pure n-alkane. The overall yields of the desulfurization reaction were good, especially considering the low solubility of linear long-chain alkanes even in hot cyclohexane.

The linear alkanes were recrystallized from hexane (Table 4). The purity of all compounds was >93%, and the melting points of the synthetic linear alkanes are in agreement with the ones reported in the literature. No attempts were made to desulfurize 6e because of the expected solubility problems. All methyl branched alkanes 2 and their precursors 6 were significantly more soluble in cyclohexane. The desulfurization of these compounds was therefore relatively easy, less hazardous, and only one desulfurization step was usually required to obtain desired alkanes 2 (Table 4). The high solubility of these compounds made it impossible to recrystallize them from n-hexane. We were able to obtain sufficiently pure samples of these alkanes by recrystallization from acetone (as determined by a combustion analysis). However, the HTGC analysis showed that all the compounds that had been recrystallized from acetone had a lower purity (74–93%) than those recrystallized from hexane.

High-temperature gas chromatography

A fast analytical method for the characterization of synthetic alkanes 2 and for verification of their purity was also needed during this study. Conven-
tional analytical methods such as NMR, FT-IR and a combustion analysis fail to detect even significant impurities of higher homologs and are therefore only of limited value for the characterization of homologous alkanes. HTGC has been extensively used to analyze petroporphyrins\textsuperscript{25-37} and natural wax mixtures.\textsuperscript{4,8,38,39} We successfully used HTGC to analyze the purity of synthetic alkanes 2 in this study.

**Experimental**

1,18-Dibromoocadecane (4e) was synthesized by Li2CuCl4-mediated coupling as described earlier.\textsuperscript{40} All methylbranched dibromides 4 were synthesized by using standard reactions. 1,ω-Dibromo-3-methylalkanes 4g and 4h were respectively synthesized from 5-oxo-hexanoic acid and 7-oxo-octanoic acid. 7-Oxo-octanoic acid was available from commercial sources, whereas 5-oxo-hexanoic acid was prepared from 5-oxo-hexanenitrile. After protecting the acid function of 5-oxo-hexanoic acid and 7-oxo-octanoic acid by esterification, the branching point was created at the position of the carbonyl C-atom by a Wittig-Horner-Emmons reaction with triethyl phosphonoacetate. Reduction of these dibromides with lithium aluminum hydride and subsequent hydrogenation yielded the mixed 3-methyl-heptanediol 4i and 3-methyl-nonanedioic acid 4j.

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**General Procedure for the Preparation of α,ω-Bis(dithianyl)alkanes 1a-c (Table 1).** A 0.58-ml amount (2.02 m in hexane) of butyllithium was slowly added to a solution of 132 mg (1.1 mmol) of 1,3-dithiane (3) and 5 mg of triphenylmethane in 15 ml of anhydrous THF at −45°C. The mixture was stirred at −45 to −30°C for 2 h. A solution of 0.5 mmol each of α,ω-dibromides 4a-c in 5 ml of anhydrous THF was added to the 2-lithio-1,3-dithiane solution, and the mixture was stored at −10°C for 12 h. The red color of the indicator vanished immediately while adding α,ω-dibromides 4a-c. The reaction was quenched with 2 ml of water, and THF was evaporated under reduced pressure. A saturated NaCl solution (5 ml) was added, and the mixture was extracted with five 5-ml portions of dichloromethane. The combined organic phases were dried over anhydrous MgSO4, and the solvent was evaporated under reduced pressure. Each product was obtained after thin-layer chromatography (silica gel, hexane: dichloromethane = 2:1).

**General procedure for the preparation of α,ω-branched bis(dithianyl)-alkanes 1d-h (Table 1).** 1,3-Dithiane (3) was lithiated as just described. Each dibromide 4d-h was added to the solution of 2-lithio-1,3-dithiane at −15 to −10°C, and the reaction mixture was stored at the same temperature for 12 h. The red color of the indicator vanished immediately while adding the dibromide. The workup of the reaction mixture was the same as that just described. Each product was obtained after thin-layer chromatography (silica gel, hexane: dichloromethane = 2:1).
alkylated α,ω-bis(dithianyl)-alkanes 6 (Table 2 and 3). Dithianes 1 were lithiated with butyllithium (3 eq.) as already described at the temperature listed in Table 2 (−15 to −10°C). Alkyl bromide 5 in anhydrous THF (5–10 ml) was added to a solution of 2-lithio-1,3-dithiane at −15 to −10°C, and the mixture was stored at −15 to −10°C for 12 h. The red color of the indicator vanished shortly after adding alkyl bromide 5. The workup of the reaction mixture was the same as that already described. 

**Monoalkylated products.** 7a: NMR δH (CDCl3): 0.89 (3 H, triplet, J = 6.6 Hz, CH3), 1.11–1.80 (65 H, m, alkyl-CH2), 2.11 (1 H, doublet, J2H2 = 12.5 Hz, quintet, J = 3.5), 2.38–2.46 (8 H, m, SCH2), 3.64 (1 H, triplet, J = 5.6 Hz, SCH3). NMR δC (CDCl3): 18.40 (CH3), 21.96, 22.48, 23.67, 29.22–29.67, 30.37, 30.40, 30.60, 31.78, 32.72 (CH3), 32.91, 35.31, 35.24, 37.98, 47.83, 53.28 (SCS). IR νmax (KBr) cm⁻¹: 2915, 2849, 1472, 1377, 1274, 719. Anal. Found: C, 74.72; H, 12.40; S, 23.83. Calcd. for C40H78S4: C, 74.92; H, 12.70; S, 23.38.

**Bisalkylated Products.** 6a: NMR δH (CDCl3): 0.67 (6 H, ‘‘triplet’’, J = 5.6 Hz, CH3), 0.84 (12 H, m, alkyl-CH2), 1.13–1.60 (96 H, m, CH2), 1.78–2.06 (12 H, m, 2.80 (8 H, ‘‘triplet’’, J = 6.2 Hz, CH3). NMR δC (CDCl3): 14.11 (CH3), 22.68, 24.04, 25.61 (dithiane CH2), 26.00 (SCH3), 29.25–29.83, 31.91, 38.16, 53.40 (SCS). IR νmax (KBr) cm⁻¹: 2919, 2849, 1465 (CH2 scissor), 1404 (SCH2), 721 (CH2 rocking). Anal. Found: C, 74.72; H, 12.40; S, 12.84%. Calcd. for C46H90S4: C, 74.79; H, 12.36; S, 12.86%. 6g: NMR δH (CDCl3): 0.83 (6 H, ‘‘triplet’’, J = 6.6 Hz, CH3), 0.89 (3 H, doublet, J = 5.6 Hz, CH3), 1.12–1.49 (61 H, m), 1.72–1.97 (12 H, m, 2.75 (8 H, ‘‘triplet’’, J = 5.6 Hz, SCS). NMR δC (CDCl3): 13.99 (CH3), 19.67 (CH2), 22.56, 23.91, 25.49, 25.90, 29.25–29.73, 30.74, 31.81, 33.20, 35.38, 38.01, 53.31 (SCS). IR νmax (KBr) cm⁻¹: 2915, 2849, 1471, 1377, 1272, 1238, 906, 715. Anal. Found: C, 71.90; H, 11.79; S, 16.34%. Calcd. for C46H90S4: C, 71.63; H, 11.79; S, 16.60%.

**General procedure for the desulfurization of the dialkyl α,ω-bis(dithianyl)-alkanes 6 (Table 2 and 4) and (Scheme 2).** Approximately 7.0 g of Raney nickel W-2(48) in cyclohexane was added to a mixture of 100–300 mg of dialkyl α,ω-bis(dithianyl)alkane 6 and 5 ml of cyclohexane in four portions. The mixture was refluxed for 20–30 min after each addition. The solids were separated by filtration through warm Celite and rinsed thoroughly with 150 ml of warm cyclohexane. The solvent was removed, and the desulfurization was repeated with an additional 7.0 g of Raney nickel. The solvent was removed under reduced pressure to yield a white solid that was recrystallized from hexane or purified by preparative TLC (SiO₂, hexane). 2a: IR νmax (KBr) cm⁻¹: 2918, 2848, 1466, 1376, 722. Anal. Found: C, 85.42; H, 14.59%. Calcd. for C₆₈H₁₃₄: C, 85.40; H, 14.60%. 2g: NMR δH (400 MHz, CDCl3): 0.85 (3 H, d, J = 6.4, CH3), 0.89 (6 H, triplet, J = 6.8, CH3), 1.08 (1 H, m, CH), 1.26 (72 H, s, CH2). NMR δC (100 MHz, CDCl3): 14.01 (CH3), 19.76 (CH3), 22.68, 27.13, 29.36, 29.50–29.80, 30.07, 31.95, 32.86 (CH), 37.19. IR νmax (KBr) cm⁻¹: 2919, 2849, 1472, 1464, 1377, 1274, 719. Anal. Found: C, 85.37; H, 14.53%. Calcd. for C₆₈H₁₃₄: C, 85.31; H, 14.69%.

**High-temperature gas chromatography of the synthetic alkanes.** High-temperature gas chromatographic (HTGC) analyses were performed with a modified Chrompack WCOT-Ultimetal column (20 m × 0.25 mm I.D., and 0.1 µm phase thickness) equipped with a 1.5 m × 0.55 mm I.D. deactivated stainless steel retention gap. Each analysis was run on a Hewlett-Packard model 5890 SII instrument equipped for on-column sample injection. The initial HTGC oven temperature was 134°C (for the o-xylene sample solvent), with a 1.0-min. initial holding time, then a temperature programmed at 10°C per min. to 450°C, and 5.0-min. final holding time. The carrier gas was helium that had been passed through a series of oxygen scrubbers. Reference ρ-paraffins (C₆₋C₁₀, C₁₂₋C₁₆, C₁₈₋C₂₀, C₂₂₋C₃₀, C₃₂₋C₃₄) of gas chromatographic grade where purchased from Fluka Chemical Corporation, Milwaukee, WI, U.S.A.

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