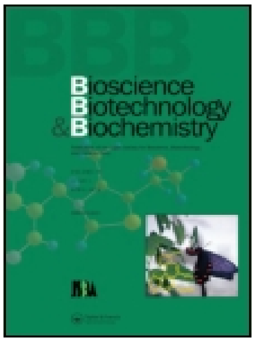

Bioscience, Biotechnology, and Biochemistry

ISSN: 0916-8451 (Print) 1347-6947 (Online) Journal homepage: http://www.tandfonline.com/loi/tbbb20

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To cite this article: Hans-Joachim LEHMLER, Robert G. BERGOSH, Mark S. MEIER & Robert M. K. CARLSON (2002) A Novel Synthesis of Branched High-molecular-weight ($C_{40}{}^{+}$) Long-chain Alkanes, Bioscience, Biotechnology, and Biochemistry, 66:3, 523-531, DOI: 10.1271/bbb.66.523

To link to this article: http://dx.doi.org/10.1271/bbb.66.523

Biosci. Biotechnol. Biochem., **66** (3), 523–531, 2002

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

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Received August 20, 2001; Accepted October 30, 2001

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 extremeophillic 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.[3–6] 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.[3] 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.[3]

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.[7] 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}.[8] 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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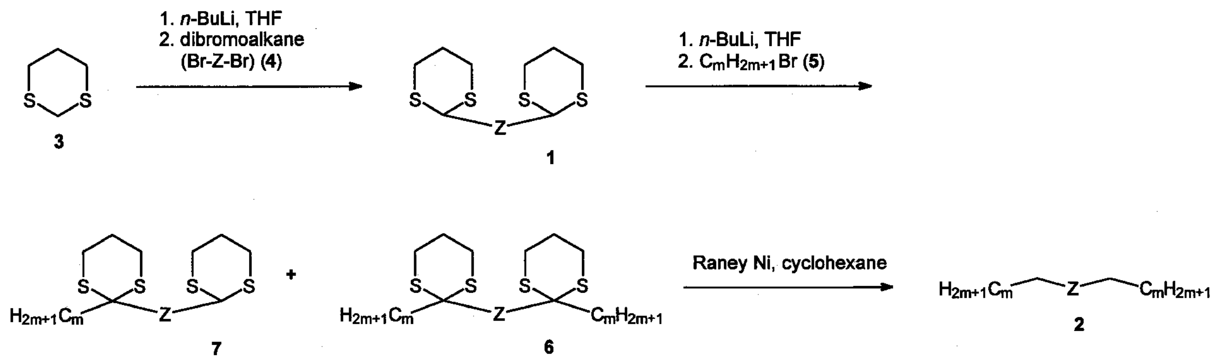
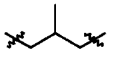
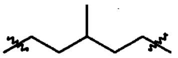
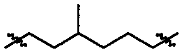
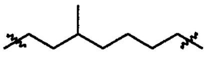
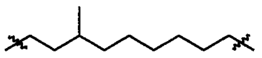
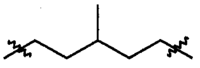
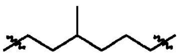
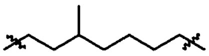
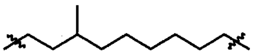


	Z
1,4a	$(CH_2)_{10}$
1,4b	$(CH_2)_{12}$
1,4c	$(CH_2)_{18}$
1,4d	
1,4e	
1,4f	
1,4g	
1,4h	

	m
5a	15
5b	16
5c	17
5d	18
5e	19
5f	22

	Z	m
2,6,7a	$(CH_2)_{10}$	22
2,6,7b	$(CH_2)_{12}$	15
2,6,7c	$(CH_2)_{12}$	16
2,6,7d	$(CH_2)_{12}$	22
6,7e	$(CH_2)_{18}$	22
2,6,7f		15
2,6,7g		16
2,6,7h		18
2,6,7i		19
2,6,7j		22
2,6,7k		17
2,6,7l		17
2,6,7m		18
2,6,7n		17

Scheme 1. Synthesis of Linear and Branched Long-chain Alkanes **2**.

als,[9-11] alkylation of β-keto esters,[12] extension of carboxylic acids with 1-morpholinocyclodecene,[13,14] Blaise ketone synthesis,[13] Wurtz coupling[12,13,15,16] 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 ($<C_{40}$).

Results and Discussion

A procedure has been needed for the rapid preparation of many individual C_{40} 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 C_{40} 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,

Table 1. Synthesis of Bis(dithianyl)alkanes **1**

Product	Temperature (lithiation) [°C]	Temperature (alkylation) [°C]	Yield [%]	Mp [°C]
1a	−45	−30	61	85
1b	−45	−10	78–79	85
1b	−10	−10	78–85	
1c	−45	−30	41	98–99
1d	−10	−10	—	
1d	−10	4	18–32	74
1e	−15 to 4	−15 to 4	70–95	oil
1f	−15	−15	57	oil
1g	−15	−15	37–54	oil
1h	−15	−15	48	oil

Table 2. Bisalkylation of Bis(dithianyl)alkanes **1**

Dithiane	1-Bromoalkane	Temperature [°C]			Monoalkylated (**7**)			Bisalkylated (**6**)	
(**1**)	(**5**)	Lithiation	Alkylation		Yield [%]	Mp [°C]		Yield [%]	Mp [°C]
1a	**5f**[a]	−10	−10	**7a**	7	oil	**6a**	50–67	57–58
1b	**5f**[a]	−20	−10	**7d**	5	37–38	**6d**	67	39
1c	**5f**[a]	23	−10	**7e**	24	31–32	**6e**	36	39
1e	**5b**[b]	−15	−15	**7g**	20	oil	**6g**	47	33–36
1e	**5d**[b]	−15	−15	**7h**	11	oil	**6h**	66	44–45
1e	**5e**[c]	−15	−15	**7i**	(13)[nc]	oil	**6i**	62	40–45
1e	**5f**[d]	−15	−15	**7j**	12	32–33	**6j**	45	56–58
1f	**5c**[c]	−15	−15	**7k**	—	—	**6k**	71	oil
1g	**5c**[c]	−15	−15	**7l**	—	—	**6l**	55	oil
1g	**5d**[c]	−15	−15	**7m**	—	—	**6m**	16	oil
1h	**5c**[c]	−15	−15	**7n**	—	—	**6n**	77	oil

[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. [nc] The compound was not fully characterized.

the first step in our approach was the alkylation of 1,3-dithiane[26] (**3**) 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]

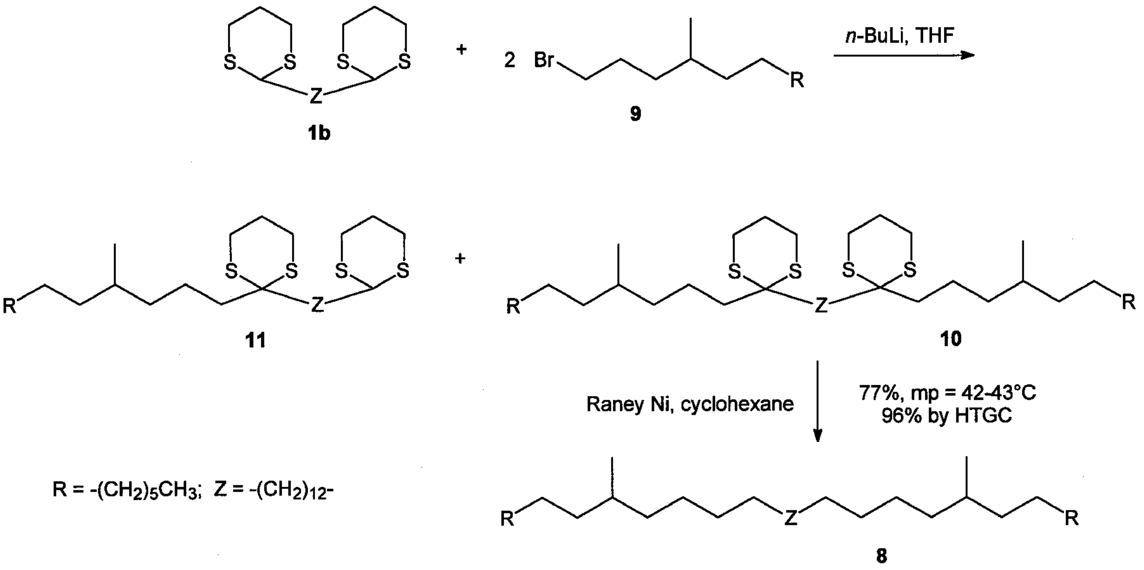
Synthesis of bis(dithianyl)alkanes 1

Bisdithianes **1** were obtained by alkylating 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-



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

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

Dithiane (**1**)	1-Bromoalkane (**5**)	eq.	*n*-BuLi[a] eq.	Monoalkylated (**7**) Yield [%]		Bisalkylated (**6**) Yield [%]	
b	**5a**	0.7	3.0	**7b**	33	**6c**	16
b	**5b**	3.0	0.8	**7c**	50	**6c**	22
b	**5b**	3.0	1.0	**7c**	39	**6c**	33
b	**5b**	3.0	1.3	**7c**	34	**6c**	40
e	**5a**	1.0	1.5	**7f**	47	**6f**[b]	16

[a] 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

tral group should be less than eighteen methylene groups.

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. Is 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*).[29,30)] 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 citronellol by following the procedure of Mori and co-workers,[23,25)] the only deviation from their synthetic approach being the direct transformation of 2,6-dimethyltetradec-2-ene to 4-methyldodecanol by reductive ozonolysis with O_3 and $NaBH_4$.

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

Product	Name	Formula	Yield* [%]	Purity[a]	Mp [°C]	Mp (lit.) [°C]
2a	Hexapentacontane	$C_{56}H_{114}$	61	95.1	97.1	90 11)
2b	Tetratetracontane	$C_{44}H_{90}$	70(85)	95.7	86.0[b]	86–86.5 43,44)
2c	Hexatetracontane	$C_{46}H_{64}$	79	99.9	88.5[c]	88–90 43,45,46)
2d	Octapentacontane	$C_{58}H_{118}$	38(78)[d]	98.5	98.8	97–100 43,47)
2f	19-Methylheptatriacontane	$C_{38}H_{78}$	86	87.4	42–45	
2g	20-Methylnonatriacontane	$C_{40}H_{82}$	71	97.4	47	
2h	22-Methyltritetracontane	$C_{44}H_{90}$	74	88.3	50–53	
2i	23-Methylpentatetracontane	$C_{46}H_{94}$	82	92.6	54–57	
2j	26-Methylhenpentacontane	$C_{52}H_{106}$	82	n.d.	58–59	
2k	21-Methyldotetracontane	$C_{43}H_{88}$	65	74.0	46–49	
2l	21-Methyltritetracontane	$C_{44}H_{90}$	71	83.2	48–50	
2m	22-Methylpentatetracontane	$C_{46}H_{94}$	72	81.8	48–51	
2n	21-Methylpentatetracontane	$C_{46}H_{94}$	65	98[e]	47–49	

* Values in parentheses are crude yields. [a] Purity determined from HTGC peak areas in the C_{15} to C_{90} range. [b] A solid state transition was observed at 71.3°C. [c] A solid state transition was observed at 74.5°C. [d] Additional 28% of impure **2d** was obtained from the filtrate, mp = 91°C. [e] Purity based on C_{10} to C_{90} 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.31,32) Methods for the desulfurization of sulfur-rich geomacromolecules are of particular interest for our synthetic approach because of the structural analogy (long hydrocarbon chains) of these compounds to bisalkylated *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,27) but nickel boride is also a suitable desulfurization agent.33,34) Gensler and coworkers have described the use of Raney nickel in cyclohexane for a synthesis of DL-methyl meromycolate,28) and Mori and co-wokers have employed Raney nickel in dioxane for the synthesis of 13,23-dimethylpenta-triacontane.30) 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. Conventional 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$^{35-37)}$ and natural wax mixtures.$^{4,6,38,39)}$ We successfully used HTGC to analyze the purity of synthetic alkanes **2** in this study.

Experimental

1,18-Dibromooctadecane (**4c**) was synthesized by Li_2CuCl_4-mediated coupling as described earlier.$^{40)}$ All methylbranched dibromides **4** were synthesized by using standard reactions. 1,ω-Dibromo-3-methyl-alkanes **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. Hydrogenation respectively yielded the mixed 3-methyl-heptanedioic acid diester and 3-methyl-nonanedioic acid diester. Reduction of these diesters with lithium aluminum hydride and subsequent bromination with triphenylphosphine/bromine gave desired 1,ω-dibromo-3-methyl-alkanes **4g** and **4h**. Two similar compounds (**4e** and **4f**) were synthesized by a similar reaction sequence. 3-Methylglutaric acid and 3-methyladipic acid were esterified, and the obtained diesters were reduced with lithium aluminum hydride in THF. We found it advantageous to hydrolyze these reaction mixtures with Rochelle salt because 3-methyl-1,5-pentanediol and 3-methyl-1,6-hexanediol were obtained in good yields.$^{41)}$ The diols were transformed into dibromides **4e** and **4f** with PPh_3/Br_2.

Lithiation of 1,3-dithiane (**3**) was performed according to the literature procedure,$^{42)}$ and THF was freshly distilled from sodium/benzophenone. All reactions were carried out under a nitrogen atmosphere. Melting point (mp) data were recorded in an open capillary and are uncorrected. The melting points of linear alkanes **2** were measured with a DuPont differential scanning calorimeter from 20°C to 120°C at 0.5°C/minute. ^{1}H- and ^{13}C-NMR spectra were measured at 200 MHz (^{1}H nucleus) and 50 MHz (^{13}C nucleus) in $CDCl_3$ as the solvent, except as otherwise noted. The chemical shifts of the new compounds were assigned with 2D-NMR techniques as far as possible. Elemental analyses were performed by Atlantic Microlab, Inc. (Norcross, Georgia, U.S.A.) or by the Microanalysis Laboratory of the School of Chemistry at University of Illinois (Urbana, Illinois, U.S.A.). Any deviation from the calculated values was less than ±0.4% for C, H and S with all the compounds. Analytical data are given for one representative compound with each series of homologous compounds.

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 $MgSO_4$, and the solvent was evaporated under reduced pressure. Each product was obtained after thin-layer chromatography (silica gel, hexane: dichloromethane = 2:1). **1a**: NMR δ_H ($CDCl_3$): 1.20–1.85 (20 H, m, alkyl-CH_2), ~1.9 (2 H, m), 2.15 (2 H, doublet, $^2J_{HH} = 11.8$ Hz, quintet, $J = 3.4$ Hz), 2.76–3.00 (8 H, m, SCH_2), 4.07 (2 H, triplet, $J = 5.6$ Hz, SCHS). NMR δ_C ($CDCl_3$): 26.05 (dithiane CH_2), 26.58 (SCH_2), 29.18, 29.32, 29.43, 30.49, 35.44, 47.66 (SCHS). IR ν_{max} (KBr) cm^{-1}: 2918, 2847, 1465 (CH_2 scissor), 1421 (SCH_2), 1276, 1177, 906, 762, 719 (CH_2 rocking). Anal. Found: C, 56.87; H, 8.96; S, 33.82%. Calcd. for $C_{18}H_{34}S_4$: C, 57.12; H, 9.06; S, 33.82%.

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. **1e**: NMR δ_H ($CDCl_3$): 0.74 (3 H, doublet, $J = 5.4$ Hz, CH_3), 1.06–1.83 (11 H, m, CH and CH_2), 1.98 (2 H, doublet, $^2J_{HH} = 14.2$ Hz, quintet, $^3J_{HH} = 3.0$), 2.58–2.93 (8H, m, SCH_2), 3.87 (2 H, triplet, $J = 6.8$ Hz, SCHS). NMR δ_C ($CDCl_3$): 19.01 (CH_3), 25.65, 30.05, 30.08, 31.87 (CH), 32.51, 33.07, 47.45 (SCS). IR ν_{max} (KBr) cm^{-1}: 2918, 1418, 1378, 1274, 1242, 1183, 907, 868, 777, 664. Anal. Found:; C, 52.19; H, 8.12; S, 39.78%. Calcd. for $C_{14}H_{26}S_4$: C, 52.12; H, 8.12; S, 39.75%.

General procedure for the preparation of di-

*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 δ_H (CDCl$_3$): 0.89 (3 H, triplet, $J=6.0$ Hz, CH_3), 1.11–1.80 (65 H, m, alkyl-CH_2), 2.11 (1 H, doublet, $^2J_{HH}=12.5$ Hz, quintet, $J=3.5$), 2.71–2.98 (8 H, m, SCH_2), 4.05 (1 H, triplet, $J=5.6$ Hz, SCHS). NMR δ_C (CDCl$_3$): 14.08 (CH$_3$), 22.65, 23.99, 25.58, 25.97, 26.57, 29.18–29.78, 30.46, 31.88, 35.43, 38.11, 47.64 (SCHS), 53.67 (SCS). IR ν_{max} (KBr) cm^{-1}: 2920, 2850, 1464 (CH$_2$ scissor), 1274, 718 (CH$_2$ rocking). Anal. Found: C, 70.02; H, 11.35; S, 18.54%. Calcd. for $C_{40}H_{78}S_4$: C, 69.92; H, 11.45; S, 18.63%. **7g**: NMR δ_H (CDCl$_3$): 0.83 (3 H, triplet, $J=6.6$ Hz, CH_3), 0.86 (3 H, double, $J=5.4$ Hz, CH_3), 1,14–1.98 (42 H, m), 2.09 (1 H, doublet, $^2J_{HH}=12.5$ Hz, m), 2.71–2.93 (8 H, m, SCH_2), 3.98 (1 H, triplet, $J=6.6$ Hz, SCHS). NMR δ_C (CDCl$_3$): 13.98 (CH$_3$), 19.46 (CH$_3$), 22.54, 23.84, 25.46, 25.88, 29.22–29.68, 30.37, 30.40, 30.60, 31.78, 32.72 (CH), 32.91, 33.51, 35.24, 37.98, 47.83, 53.28 (SCS). IR ν_{max} (KBr) cm^{-1}: 2918, 1458, 1376, 1274, 1240, 1179, 908, 868, 783, 721, 679. Anal. Found: C, 65.85; H, 10.61; S, 23.36%. Calcd. for $C_{30}H_{58}S_4$: C, 65.89; H, 10.70; S, 23.41%. *Bisalkylated Products*: **6a**: NMR δ_H (CDCl$_3$): 0.87 (6 H, "triplet", $J=5.6$ Hz, CH_3), 1.13–1.60 (96 H, m, CH_2), 1.78–2.06 (12 H, m), 2.80 (8 H, "triplet", $J=6.2$ Hz, SCH_2). NMR δ_C (CDCl$_3$): 14.11 (CH$_3$), 22.68, 24.04, 25.61 (dithiane CH$_2$), 26.00 (SCH$_2$), 29.35–29.83, 31.91, 38.16, 53.40 (SCS). IR ν_{max} (KBr) cm^{-1}: 2919, 2849, 1465 (CH$_2$ scissor), 1404 (SCH$_2$), 721 (CH$_2$ rocking). Anal. Found: C, 74.72; H, 12.40; S, 12.84%. Calcd. for $C_{62}H_{122}S_4$: C, 74.79; H, 12.36; S, 12.86%. **6g**: NMR δ_H (CDCl$_3$): 0.83 (6 H, "triplet", $J=6.6$ Hz, CH_3), 0.89 (3 H, doublet, $J=5.6$ Hz, CH_3), 1.12–1.49 (61 H, m), 1.72–1.97 (12 H, m), 2.75 (8 H, "triplet", $J=5.6$ Hz, SCH_2). NMR δ_C (CDCl$_3$): 13.99 (CH$_3$), 19.67 (CH$_3$), 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 ν_{max} (KBr) cm^{-1}: 2915, 2849, 1471, 1377, 1272, 1238, 906, 715. Anal. Found: C, 71.90; H, 11.79; S, 16.34%. Calcd. for $C_{46}H_{90}S_4$: C, 71.63; H, 11.79; S, 16.60%.

*General procedure for the desulfurization of the dialkyl α,ω-bis(dithianyl)-alkanes **6** (Table 4) and **10** (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 (SiO$_2$, hexane). **2a**: IR ν_{max} (KBr) cm^{-1}: 2918, 2848, 1466, 1376, 722. Anal. Found: C, 85.42; H, 14.59%. Calcd. for $C_{56}H_{114}$: C, 85.40; H, 14.60%. **2g**: NMR δ_H (400 MHz, CDCl$_3$): 0.85 (3 H, d, $J=6.4$, CH_3), 0.89 (6 H, triplet, J = 6.8, CH_3), 1,08 (1 H, m, CH), 1.26 (72 H, s, CH_2). NMR δ_C (100 MHz, CDCl$_3$): 14.01 (CH$_3$), 19.76 (CH$_3$), 22.68, 27.13, 29.36, 29.60–29.80, 30.07, 31.95, 32.86 (CH), 37.19. IR ν_{max} (KBr) cm^{-1}: 2919, 2849, 1472, 1464, 1377, 1274, 719. Anal. Found: C, 85.37; H, 14.53%. Calcd. for $C_{40}H_{82}$: 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 *n*-paraffins (C_{40}-C_{42}, C_{44}, C_{46}, C_{48}, C_{50}, C_{54}, C_{56}, C_{58} and C_{60}) of gas chromatographic grade where purchased from Fluka Chemical Corporation, Milwaukee, WI, U.S.A.

Acknowledgments

We thank Chevron Petroleum Technology Company (La Habra, CA, U.S.A.) for funding this project, and M. M. Pena for the HTGC analyses. One of us, HJL, thanks Drs. D. S. Watt and M. S. Meier for providing support and laboratory facilities.

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