Intramolecular Hydrogen Transfers in Vinyl Chloride Polymerization: Routes to Doubly Branched Structures and Internal Double Bonds

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ABSTRACT: During the preparation of poly(vinyl chloride) (PVC) under low monomer pressures, intramolecular hydrogen transfers ("backbites") lead to the formation of small amounts of 1,3-bis(2-chloroethyl) branch (DEB) structures, as well as allylic chloride segments resulting from 1,6 shifts. The presence of these structural defects was established by the ^{13}C NMR spectra (recorded at 125.77 MHz) of dechlorinated PVC specimens made by organotin hydride reduction. At 55−80 °C, the two backbites leading to DEB groups differ substantially in relative rate, in that the backbiting:addition rate ratio is larger for the second backbite by a factor of 15−16, irrespective of temperature. No convincing evidence was obtained for the presence of a chlorinated 2-ethyl-*n*-hexyl branch (EHB) segment resulting from double backbiting by an alternative route. Backbiting effects on dichlorobutyl branch concentrations and on chain transfer to monomer are discussed and quantified, and the synthesis of models for dechlorinated DEB and EHB structures is described.

Short-chain branches can be formed during the preparation of many important addition polymers such as low-density polyethylene and ethylene copolymers.[1] The structures, concentrations, and distributions of these branches are thought to have important effects on the solid-state physical properties and morphologies of the resins in which the branches occur. Thus the identification and enumeration of the short branches has been the focus of much research.[1]

In the case of poly(vinyl chloride) (PVC), the short-chain branches are of interest for an additional practical reason, which relates to the possibility that the branch-point carbon is attached to a chloro substituent. The resultant tertiary chloride structures are believed by many researchers to contribute very significantly to PVC instability, in that they serve as starting sites for thermal dehydrochlorination.[2]

In low-density polyethylene, *n*-butyl branches are formed by a mechanism, apparently proposed first by Roedel,[3] which involves intramolecular hydrogen abstraction ("backbiting") by the propagating macroradical, via a cyclic transition state that is six-membered in size.[1a,b,d] An analogous process, shown at the top of Figure 1, operates during the polymerization of vinyl chloride (VC).[2,4] In that case, continual head-to-tail addition of monomer to the radical formed by intramolecular transfer (**1**) gives, in low concentration,[4] a dichlorobutyl branch structure (BB) containing tertiary chloride. However, when **1** has reacted with only one monomer molecule, the resulting radical (**2**) has other options (in theory, at least) for further transformation. Like its precursor, P$^\bullet$, **2** may experience six-center backbiting, but now in one or both of two ways, to generate radical **3** and/or radical **4**, whose subsequent addition to monomer should produce a 1,3-diethyl branch pair (DEB) or a 2-ethyl-*n*-hexyl branch arrangement (EHB). First suggested to intervene in ethylene polymerization,[5] analogous backbites have now been stated explicitly to occur in that system on the basis of ^{13}C NMR studies carried out by numerous workers.[1a,b,6] The possibility of successive backbites in PVC synthesis has been noted before, as well,[7] and the likely thermal lability of the DEB and EHB structures, resulting from their incorporation of two tertiary chloride moieties, has been pointed out.[7] Yet no detailed evidence for the presence of these structures has been reported thus far.

In VC polymerization, there is another potential process that also starts with backbiting but produces a different kind of structure having low thermal stability.[7] This process involves the abstraction of methylene hydrogen (eq 1) to form a rearranged radical (**5**) that

$$\mathrm{P}^\bullet \rightarrow \underset{\mathbf{5}}{-\mathrm{CHClC}^\bullet\mathrm{HCHCl}}\sim\mathrm{CH_2CH_2Cl} \qquad (1)$$

can react with VC by chlorine-atom β scission in order to give an unstable internal allyl (IA) array (eq 2). The

$$\mathbf{5} + \mathrm{VC} \rightarrow \underset{\mathrm{IA}}{-\mathrm{CH}=\mathrm{CHCHCl}-} + \mathrm{ClCH_2C}^\bullet\mathrm{HCl} \qquad (2)$$

intermolecular counterpart of reaction 1 is very likely to be involved in the polymerization,[8] and the donation of Cl$^\bullet$ to VC from radicals formed by H$^\bullet$ abstraction is now known to be an important process for chain transfer to the monomer.[8,9] Yet the relative importance of reaction 1 and its intermolecular analogue has not been disclosed.

We now report information that has a bearing on this question and on the possible presence in PVC of the "double backbiting" structures, DEB and EHB. Our experimental procedure has involved the reductive dechlorination of PVC samples with tri-*n*-butyltin hydride and analysis of the resulting polymers by ^{13}C

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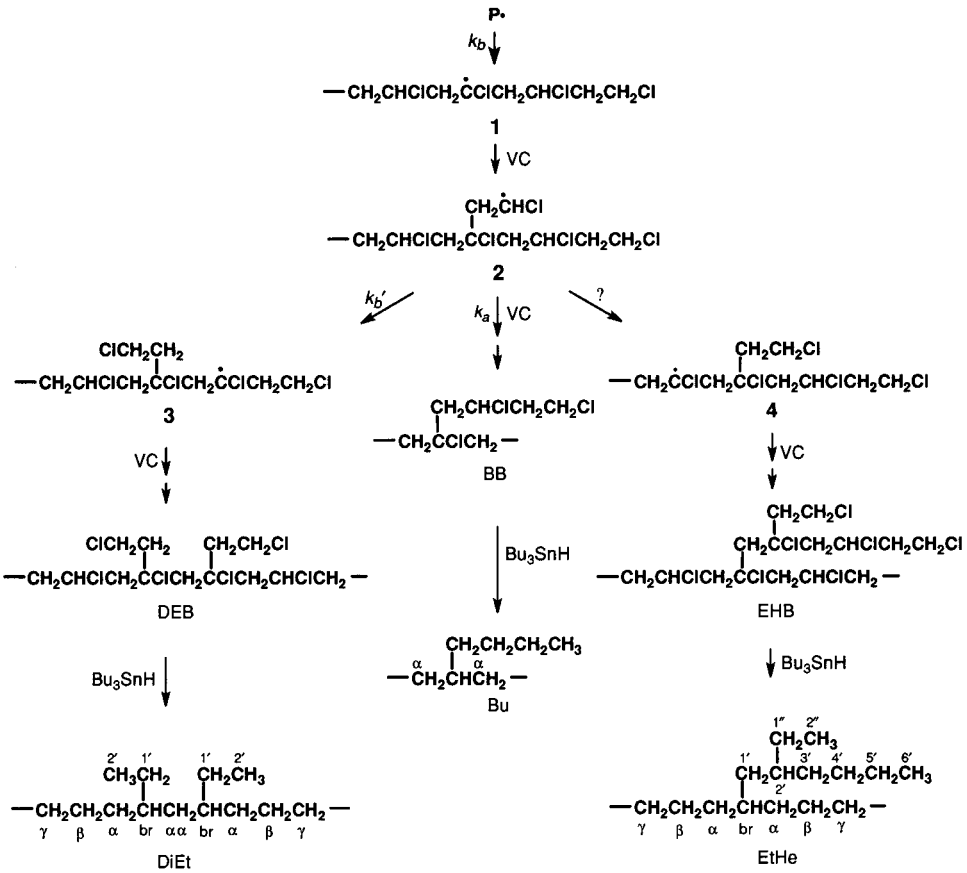


Figure 1. Creation and reduction of branch structures formed by backbiting during the polymerization of VC, where P• is the head-to-tail macroradical, and the *k*s are rate constants.

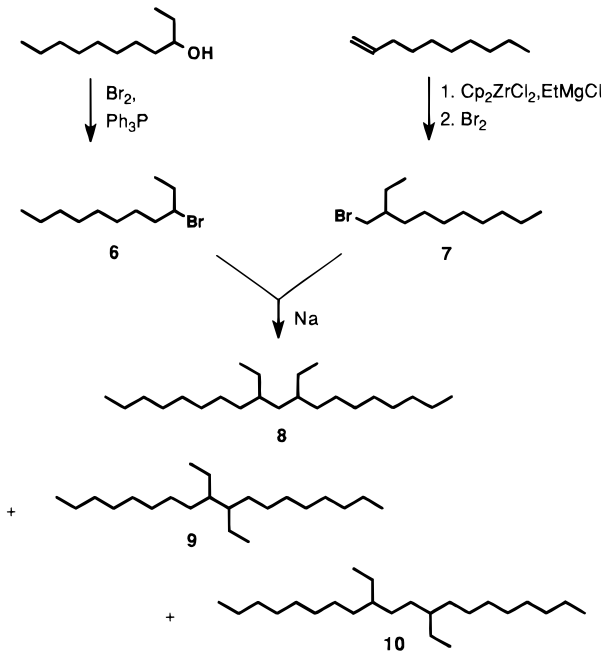
NMR.[7] If such an approach reveals that the DiEt and EtHe segments in Figure 1 have been formed, then the existence of their chlorine-containing progenitors obviously can be inferred. Moreover, the ^{13}C NMR spectrum of a cyclic structure also created by the reduction can reveal the presence of IA groups made by reactions 1 and 2.[9] The argument that supports this conclusion is reserved for a later section.

Of crucial importance in our NMR studies were the chemical shifts of the DiEt and EtHe carbons and the carbons in the aforementioned product expected to derive from IA. These shifts were determined very accurately from the spectra of model compounds.

Results and Discussion

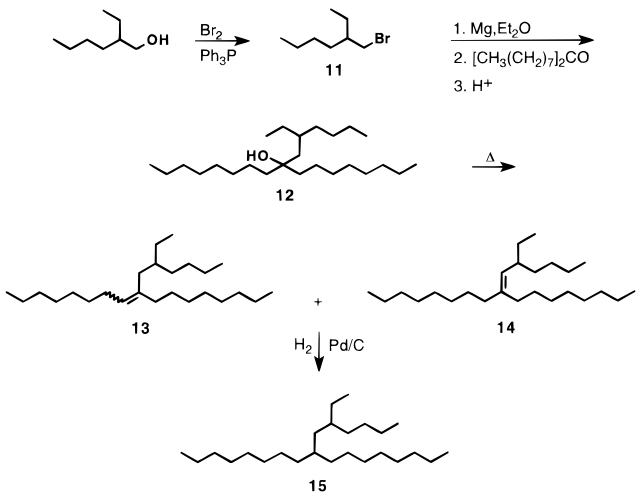
Models for the DiEt and EtHe Structures. Prior to this investigation, ^{13}C chemical shifts had been reported for two models for structure DiEt (5,7-diethyldocosane and 5,7-diethyldodecane)[6d,e,10] and one model for structure EtHe [12-(2-ethyl-*n*-hexyl)tricosane[6d,e]]. Unfortunately, the NMR sample conditions (solvent and temperature) used to obtain those data differed significantly from those used by us in all of our previous NMR studies of reduced PVC. Thus we needed to acquire some model specimens of our own in order to measure the reference shifts that were needed for our work. Synthetic procedures for the models used earlier[6d,e,10] apparently had not been published, but in ref 6d these procedures were said to be available to the reader. Nevertheless, we could not obtain them.[11] Thus we prepared the requisite models by applying methods that we devised.

Scheme 1



Compound **8**, the DiEt model, was made by the route in Scheme 1. One of the needed precursors, bromoalkane **6**, was obtained from the corresponding alcohol by adapting a well-known general procedure.[12] The other precursor, bromoalkane **7**, was acquired by adapting an elegant two-step sequence that involves the Cp_2ZrCl_2-promoted addition of a Grignard reagent to an alkene, followed by reaction of the adduct with an

Scheme 2



electrophile that introduces a halo substituent.[13] A Wurtz reaction of **6** and **7** then gave the cross-coupling product **8**, together with the dimers **9** and **10** resulting from homocoupling. The isolation of **8** was not attempted and, in fact, was not required, because the diagnostic chemical shifts of this substance were determined very easily from the ^{13}C NMR spectrum of the ternary mixture of hydrocarbons. Resonance assignments in that spectrum were confirmed by comparisons with the spectra of authentic samples of **9** and **10** that were made by the magnesium-promoted homocoupling of **6** and **7**, respectively.

Our EtHe model, **15**, was prepared by the method shown in Scheme 2. The last three steps in this sequence parallel those used by Freche et al.[14] in order to obtain a series of 12-(*n*-alkyl)tricosanes. Bromoalkane **11**, acquired by bromodehydroxylation (cf. the preparation of **6**), was converted into a Grignard reagent that was allowed to react with 9-heptadecanone in the conventional way. The product, alcohol **12**, was not isolated but was transformed into an alkene mixture by thermal dehydration under vacuum. The alkenes were identified tentatively as **13** and **14** on the basis of their mass spectra. However, their exact structures actually were inconsequential, as their mixture was readily reduced to **15** by catalytic hydrogenation. The sample of **15** thus obtained contained minor amounts of 9-heptadecanone and 9-heptadecanol (**16**) as impurities. Their presence was established by a ^{13}C NMR spectrum which also showed that their distinctive resonances did not interfere with those of **15**. The reference sample of **16** that was needed for spectral comparisons was prepared by reducing the ketone with lithium borohydride.

Table 1 compares some predicted shift values with the diagnostic ^{13}C shifts of models **8** and **15**. The predictions were made by using temperature-corrected Grant−Paul parameters[15] in order to modify the chemical shifts of poly(ethylene-*co*-1-alkene)s[16] containing ethyl or *n*-hexyl branches. The basic information resorted to here seemed particularly appropriate for our purposes, because both the temperature corrections[15] and the starting shifts[16] had been determined under conditions of solvent and temperature that resembled ours rather closely. In the case of the DiEt structure, all of the original shifts used for predictions were those of the ethyl-branched copolymer. Shifts of that copolymer also were used to predict the shifts of the EtHe-2′, -3′, -1″, and -2″ carbons (for nomenclature, see Figure 1).

Table 1. ^{13}C Shifts of Possible Structures Resulting from "Backbiting" and Subsequent Reductive Dechlorination

	δ,[a] ppm vs Me_4Si		
carbon	predicted[b]	model	polymer
DiEt-1′	27.22	27.05,[c] 27.13[c]	26.99, 27.06
DiEt-2′	11.25	10.98, 11.01	10.96, 11.00
DiEt-br	37.17	37.38, 37.42	37.30, 37.34
DiEt-αα	38.54	39.15	39.05
DiEt-α	34.52	34.43, 34.46	hidden
DiEt-*β*	27.36	27.19,[c] 27.23[c]	27.13, 27.16
EtHe-1′	39.05	39.53	
EtHe-2′	37.17	37.22	
EtHe-3′	34.09	33.97	
EtHe-4′	29.87	29.76[c]	
EtHe-5′	23.53	23.48	
EtHe-6′	14.35	14.16	
EtHe-1″	27.22	26.98[c]	
EtHe-2″	11.25	10.98	
EtHe-br	35.74	35.79	
EtHe-α	35.03	34.81, 34.88	
EtHe-*β*	27.48	27.07,[c] 27.12[c]	
EtHe-*γ*	30.68	30.55	
MCP-1	39.7	40.74[d]	40.61
MCP-2,5	32.9	33.21[d]	33.12
MCP-3,4	25.4	25.66[d]	25.59
MCP-α	36.3	36.68[d]	36.56
MCP-*β*	29.1	29.11[d]	28.99

[a] Determined at 100 °C (unless noted otherwise) and 125.77 MHz from 15−20% (w/v) solutions in 1,2,4-trichlorobenzene/*p*-dioxane-d_8 (ca. 4:1 v/v). [b] See text for discussion. [c] Tentative assignment. [d] Determined at 110 °C.

The experimental shifts of the models are in good general agreement with the predicted values. They also agree satisfactorily with the shifts of similar models measured under other conditions.[6d,e,10] Because of the mutual close proximity of the DiEt-1′ and -*β* peaks, the assignments made for those resonances might require transposition. An analogous statement applies to the EtHe-1″ and -*β* assignments. The presence of both the meso and the racemic stereoisomers presumably caused the doubling found for most of the DiEt signals. However, the EtHe-α and -*β* doubling must be ascribed to the presence of the single chiral center. In this regard, an analogy is provided by the magnetic nonequivalence of the isopropyl methyl carbons of $(CH_3)_2CHCH_2CH(CH_3)CH_2CH_3$.[17]

Identification of Doubly Branched Structures in Reduced PVC. Samples of PVC were made previously[8] at constant VC pressures that ranged from 59% to 100% of the pressure at saturation. After reductive dechlorination, the polymers made at the lowest pressures displayed several DiEt resonances in their ^{13}C NMR spectra. The chemical shifts of those signals are given in Table 1, and the resonances are assigned in Figure 2B, which shows parts of the spectrum of a resin that is described in the figure caption. Figure 2B also contains assignments for the resonances of "MCP" (monoalkylcyclopentane) carbons (see below) and carbons denoted in Figure 3,[18] while Figure 2A shows, for comparison, most of the DiEt signals of model compound **8**.

In Figure 2B, the DiEt-br and -2′ peaks can be identified easily. The DiEt-αα resonance obviously is present as well, notwithstanding the possibility, currently considered unlikely, that its assignment and that for the Cl-*β* signal need to be interchanged. Assignments made for the DiEt-*β* and -1′ resonances are

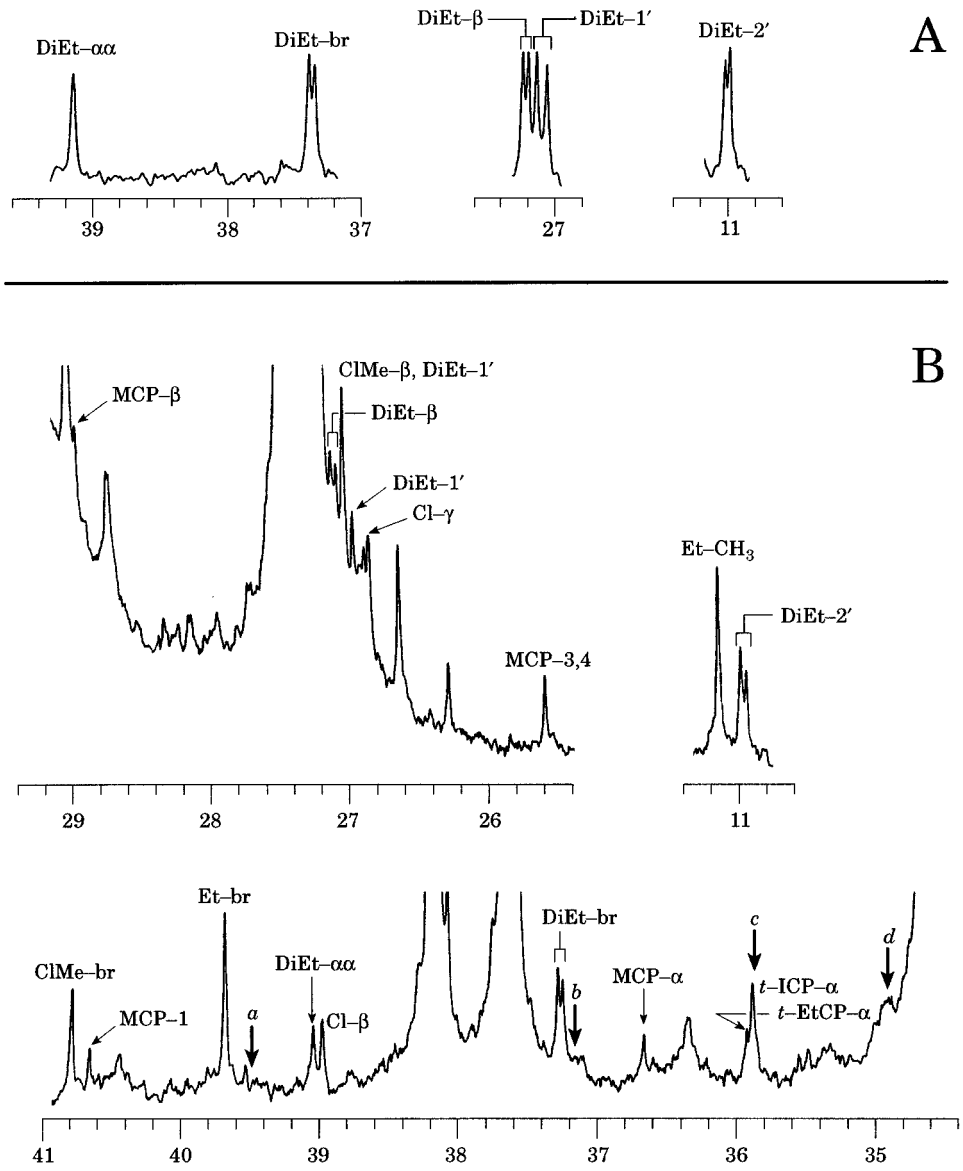


Figure 2. Proton-decoupled ^{13}C NMR partial spectra [125.77 MHz, 100 °C, 1,2,4-trichlorobenzene/*p*-dioxane-d_8 (ca. 4:1 v/v)] of (A) model compound **8** and (B) a Bu_3SnH-reduced PVC specimen made at 55 °C with a VC pressure at 59% of the pressure at saturation. Because of inefficient agitation, the VC concentration in the polymer particles was less than the equilibrium value and, as a result, the $\bar{M}_n$ of the unreduced polymer (2.5×10^4) was abnormally low (cf. ref 8). Numerical scales denote chemical shifts in ppm vs Me_4Si; arrows *a*–*d* show the approximate shift positions of EtHe carbons that are listed in Table 1.

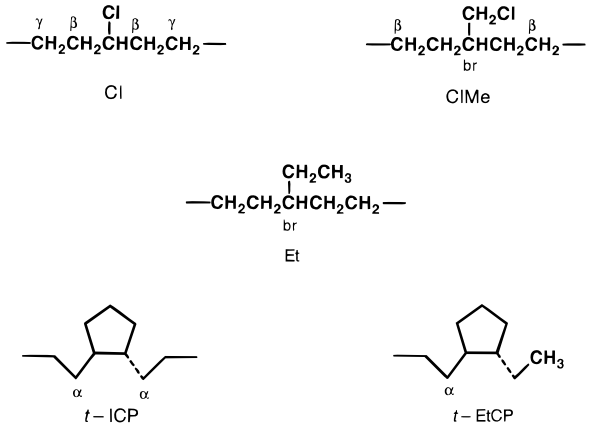


Figure 3. Some of the structures found previously[7,19–22] in Bu_3SnH-reduced PVC.

consistent with the central spectrum of Figure 2A, despite the apparent coincidence of a DiEt-1′ signal with the ClMe-β peak. That the ClMe structure was indeed present followed from the observation of all of its unique absorptions,[19] including the ClMe-br resonance identified in Figure 2B. The two DiEt-α peaks did not appear in the polymer spectrum, but their absence was not surprising, because they were expected to be obscured by the relatively strong α-carbon resonance[7] (not shown) of the Bu structure in Figure 1.

Some of the polymer spectra containing the DiEt resonances in Table 1 also exhibited two weak shoulders (not shown in Figure 2B) near 30.6 ppm (at 30.61 and 30.65 ppm, for example). One or both of these shoulders might have arisen, at least in part, from DiEt-γ carbons, for which our predicted shift value is 30.40 ppm. It is important to note, however, in this context that the cis isomer of the EtCP structure in Figure 3 also would have given a peak at ca. 30.6 ppm.[22] Our purified samples of **9** and **10** produced only singlets in the 30.5–30.6 ppm region, but the mixture of **8**, **9**, and **10** elicited signals at 30.55 and 30.57 ppm. This doubling could

have resulted from the presence of two DiEt-γ resonances or from a difference in the shifts of singlets associated with different compounds.

In contrast to our NMR observations of the DiEt structure, we have not been able to establish the presence of the EtHe moiety in reduced samples of PVC. Perhaps the strongest evidence for the absence of that structure is the failure of the EtHe-1′ resonance to appear at its expected position, which is denoted by arrow *a* in Figure 2B. At our field strength of 125.77 MHz, this resonance should have been well-resolved from both of its neighbors, whose intensities give no evidence for its presence as a coincident peak. Moreover, when the NMR solvent was changed from 1,2,4-trichlorobenzene to tetrachloroethane-d_2, no new resonances emerged from the DiEt-αα and Et-br signals. Clear evidence for the presence of the EtHe-2′ singlet (arrow *b*) and the EtHe-α doublet (arrow *d*) also is lacking from Figure 2B, and the ill-defined *b* and *d* absorptions in that figure were either very weak or undetectable in the spectra of other reduced PVC specimens that also contained significant amounts of structure DiEt. The EtHe-br resonance (arrow *c*), if present, would have overlapped the *t*-ICP-α/*t*-EtCP-α composite peak. That peak may have an upfield shoulder in Figure 2B, but such a shoulder did not appear in the spectra of similar specimens.

Rough estimates based on our carbon spectra indicate that the EtHe concentration in our polymer samples always was less than that of the DiEt structure by a factor of 3−4, at least. This result contrasts strikingly with a predicted DiEt:EtHe ratio of 1:1 that was deduced for low-density polyethylene (LDPE) from statistical calculations.[23] Similar calculations for PVC obviously would be of interest. However, the apparent absence of the EHB structure from that polymer can perhaps be rationalized in a simplistic way by noting that radical **2** may encounter more nonbonded repulsions when it attempts to backbite from its polymeric moiety (to give **4**), rather than from its much less bulky dichloro-*n*-butyl branch (to generate **3**).

The ^{13}C NMR spectra of LDPE samples frequently contain a weak resonance near 8 ppm that can be assigned to the methyl C of an ethyl branch attached to a quaternary center.[1b−d,6b,e,f,h] This resonance did not appear in the spectra of any of our reduced specimens.

Concentrations of the Branch Structures Formed by Backbiting. From Figure 1, it follows that, under steady-state conditions, the formation rates of the BB and DEB structures will be given by eqs 3 and 4, where

$$\mathrm{d[BB]/d}t = k_b k_a[\mathrm{P^\bullet}][\mathrm{VC}]/(k_a[\mathrm{VC}] + k_b') \quad (3)$$

$$\mathrm{d[DEB]/d}t = k_b k_b'[\mathrm{P^\bullet}]/(k_a[\mathrm{VC}] + k_b') \quad (4)$$

$$\mathrm{d[PVC]/d}t = k_p[\mathrm{P^\bullet}][\mathrm{VC}] \quad (5)$$

molar concentrations are denoted by brackets. Since most of the P• radicals undergo tail addition to monomer, the rate of polymerization can be described by eq 5, where k_p is the conventional rate constant for propagation, and [PVC] is the concentration of polymerized VC units. The BB and DEB concentrations per monomer unit ($\bar{\rho}_{BB}$ and $\bar{\rho}_{DEB}$) then are given by eqs 6 and 7, which when added or divided yield eqs 8 and 9, respectively. Division of eq 9 by eq 8 produces eq 10.

$$\bar{\rho}_{BB} = \frac{\mathrm{d[BB]/d}t}{\mathrm{d[PVC]/d}t} = \frac{k_b k_a}{k_p(k_a[\mathrm{VC}] + k_b')} \quad (6)$$

$$\bar{\rho}_{DEB} = \frac{\mathrm{d[DEB]/d}t}{\mathrm{d[PVC]/d}t} = \frac{k_b k_b'}{k_p[\mathrm{VC}](k_a[\mathrm{VC}] + k_b')} \quad (7)$$

$$\bar{\rho}_{BB} + \bar{\rho}_{DEB} = k_b/k_p[\mathrm{VC}] \quad (8)$$

$$\bar{\rho}_{DEB}/\bar{\rho}_{BB} = k_b'/k_a[\mathrm{VC}] \quad (9)$$

$$\bar{\rho}_{DEB}/\bar{\rho}_{BB}(\bar{\rho}_{BB} + \bar{\rho}_{DEB}) = k_b' k_p/k_b k_a \quad (10)$$

Because of the structural resemblance of P• to radical **2**, the values of k_a and k_p should be similar. Hence the magnitude of the right-hand side of eq 10 should be an approximate measure of the relative rates of backbiting by radical **2** and P•. The DiEt concentration (per monomer unit) obviously equals $\bar{\rho}_{DEB}$ (when the concentrations of incompletely reduced[19] DEB structures are low enough to be ignored), and $\bar{\rho}_{BB}$ can be equated to the sum of the concentrations of the fully reduced segment, Bu, and another reduced structure, $-CH_2CH(CH_2CH_2CH_2CH_2Cl)CH_2-$, containing residual halogen.[4,19] Therefore, from the complete spectrum shown in part in Figure 2B, values of $\bar{\rho}_{DEB}$ and $\bar{\rho}_{BB}$ could be deduced for the original (unreduced) polymer. They were found to be $0.3_3 \times 10^{-3}$ and 4.8×10^{-3}, respectively, and they lead to a value of 13 for $k_b'k_p/k_bk_a$ ($\approx k_b'/k_b$) when they are used in eq 10. An approximate k_b'/k_b value of 17 was obtained in the same manner for another polymerization performed at 55 °C with a constant VC pressure at 59% of saturation. In this case, agglomeration resulting from inefficient agitation led to a PVC $\bar{M}_n$ value of 2.9×10^4 (cf. the information in the caption for Figure 2B), and the respective values of $\bar{\rho}_{DEB}$ and $\bar{\rho}_{BB}$ were $0.3_0 \times 10^{-3}$ and 4.1×10^{-3}. The mean k_b'/k_b value of 15 ± 2 for 55 °C confirms an expectation arising from conclusions reached about backbiting rates during LDPE synthesis,[5,23a] namely, that the second backbite would be significantly faster than the first. The experimental rate ratio for VC polymerization is greater, though, than the theoretical ratios of 2−6 (at 200−400 °C) that were deduced for ethylene polymerization from rotational isomeric state statistics.[23a] This difference could be due mostly to structural dissimilarities, but it may result also, in part, from the temperature discrepancy and a k_p/k_a ratio that actually is slightly larger than 1, owing to steric hindrance in the addition of radical **2** to monomer.

The backbiting reactions of P• and **2** are very similar with regard to reactants, transition states, and products. Thus, by analogy with LDPE,[23a] the inequality of k_b and k_b' can reasonably be ascribed to differences in conformer populations. In the case of ethylene polymerization, the conformational statistics predict a very small effect of temperature on the rate ratio for backbiting[23a] (from Figure 4 of ref 23a, we estimate a maximum conformational contribution of only 1.8 kcal/mol to the difference between the Arrhenius activation energies of the first and second backbites). Furthermore, the activation energies associated with k_a and k_p should be nearly equivalent. Therefore, one might expect the value of $k_b'k_p/k_bk_a$ to be relatively insensitive to temperature changes. This hypothesis was validated by the data obtained for a PVC specimen that was prepared at 80 °C under a constant monomer pressure which, as

before, was 59% of the pressure at saturation.[8] In this case, however, agglomeration did not affect the VC concentration in polymer particles, and a $k_b'k_p/k_bk_a$ value of 16 was derived from the values of $\bar{\rho}_{DEB}$ and $\bar{\rho}_{BB}$, which were $0.3_3 \times 10^{-3}$ and 4.4×10^{-3}, respectively. Our $k_b'k_p/k_bk_a$ values for 80 and 55 °C are considered to be identical within the error limits of our measurements.

In a previous investigation,[4] good straight lines were obtained from plots of $\bar{\rho}_{BB}$ vs $[VC]^{-1}$ that were constructed with data of Hjertberg and Sörvik[24] for polymers made at various temperatures. From eq 8 it is apparent that such linearity can ensue only when $\bar{\rho}_{DEB}$ is small. Rearrangement converts eq 10 into eq 11,

$$\bar{\rho}_{DEB} = \frac{(\bar{\rho}_{BB})^2}{(k_bk_a/k_b'k_p) - \bar{\rho}_{BB}} \qquad (11)$$

which was used to calculate values of $\bar{\rho}_{DEB}$ from the Hjertberg–Sörvik[24] $\bar{\rho}_{BB}$ data and $k_b'k_p/k_bk_a$ values of 15 or 16. The results showed that $\bar{\rho}_{DEB}$ was never greater than 0.1×10^{-3}. Thus its inclusion would have had only minor effects on the slopes of the linear plots in Figures 1 and 2 of ref 4. Nevertheless, its introduction should slightly improve the regression fits of some of those plots by increasing the highest branch concentrations.

A straight line also resulted when the $\bar{\rho}_{BB}$ values of some polymers made at 40 °C in solution were plotted vs $[VC]^{-1}$.[4] For this series of samples, the values of $10^3(\bar{\rho}_{BB})$ range from 0.9 to 5.6,[4] and the DEB concentrations ($\times 10^3$) found from eq 11 (with $k_b'k_p/k_bk_a$ set equal to 15) range from 0.01 to 0.5. A double-regression plot of eq 8 made with these data has an R^2 value of 0.97 and gives a k_b/k_p ratio of 3.0×10^{-3} M. This ratio compares favorably with the k_b/k_p value of 2.5×10^{-3} M found previously[4] for heterogeneous polymerizations at 40 °C. In heterogeneous media, the k_b/k_p ratio actually would be larger than it is in solution if propagation were controlled by diffusion at high conversions under heterogeneous conditions.[4] Thus our revised k_b/k_p ratio for solution polymerization strongly supports our earlier arguments[4] against the occurrence of diffusion-controlled propagation.

Inversion converts eq 7 into eq 12, which can be used to calculate $\bar{\rho}_{DEB}$ as a function of VC concentration if

$$(\bar{\rho}_{DEB})^{-1} = \frac{k_p[VC]}{k_b}\left\{\frac{k_a[VC]}{k_b'} + 1\right\} \qquad (12)$$

the k_p/k_b and k_a/k_b' values are available for the temperature of interest. These values can be obtained conveniently from eqs 8 and 9 when the requisite data have been collected for one or more PVC samples.

Because $\bar{\rho}_{DEB}$ depends in part on $[VC]^{-2}$, rather than exclusively on $[VC]^{-1}$ (see eq 7), its increase with conversion is more rapid than those of the other thermally labile defect structures.[4,8] For this reason, the DEB structure may substantially reduce the stability of polymer fractions that are produced after [VC] reaches low levels. On the other hand, the DEB contents of whole polymers made commercially should be relatively insignificant.

Backbiting as a Route to Internal Double Bonds. In situations that are structurally favorable, carbon-centered radicals may rearrange by 1,6 hydrogen transfers involving cyclic transition states containing seven members.[25] These rearrangements are well-known to be much faster than similar ones in which the transient rings are small. On the other hand, 1,6 shifts ordinarily are slower than analogous 1,5 shifts.[25] During VC polymerization, the 1,6 rearrangement of P•, illustrated in Figure 4, could be abnormally sluggish, because the thermodynamic stabilities of P• and radical **17** are unlikely to differ substantially.[7]

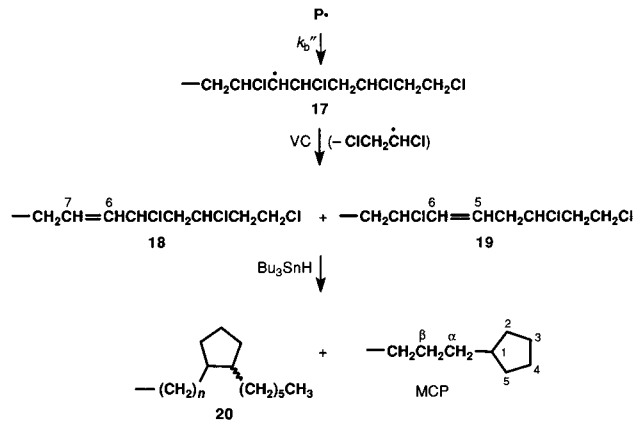
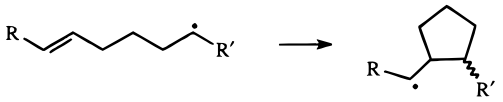


Figure 4. Creation and reduction of alkene structures formed by backbiting during the polymerization of VC, where P• is the head-to-tail macroradical, and k_b'' is a rate constant.

Radical **17** presumably can add to the monomer, but it also should be able to react with VC by β scission[8] in order to form a mixture of structures **18** and **19**. In view of the symmetry of **17** near its radical center, the yields of these two products should be virtually identical. Their reduction by Bu_3SnH should produce an equimolar mixture of **20** and the MCP structure, for reasons that will now be described.

Cyclization during reductions of PVC by Bu_3SnH involves the addition of a carbon-centered radical, formed from a C–Cl moiety, to a double bond so as to produce a five-membered ring and transfer the free electron to the α carbon atom of a ring substituent[21,22,25a] (eq 13). When the double bond is between C-6 and C-7



(as in **18**), reductive cyclization will give structure **20** exclusively. On the other hand, a double bond between C-5 and C-6 will cause the MCP terminus to become the only cyclic product. Reactivity data obtained for models[26] indicate that the chloroallyl parts of **18** and **19** will experience nearly quantitative dechlorination before cyclization occurs, and since those partial reductions must involve the same intermediate allyl species[26] (ignoring possible steric differences), both of them should yield equal amounts of 5- and 6-alkene. Accordingly, equal amounts of **20** and MCP should be formed from the (presumed) equivalent quantities of **18** and **19**. Structure **20** cannot be distinguished spectroscopically from the 1,2-bis(long alkyl)cyclopentanes which arise from the internal double bonds[21] that are formed, apparently, via intermolecular chemistry that is analogous to reactions 1 and 2.[8] In contrast, the MCP moiety is unique, and its presence can be taken as conclusive evidence for the β scission of **17** radicals that are formed by backbiting.

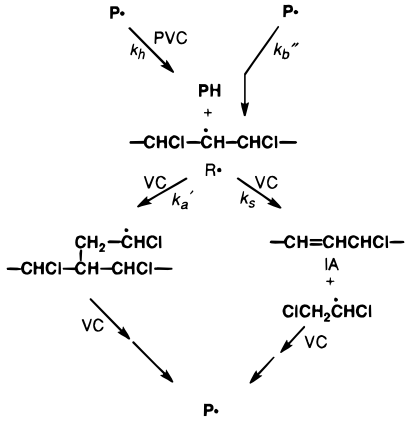


Figure 5. Auxiliary mechanism for transfer to monomer during the polymerization of VC, where P• is the head-to-tail macroradical, and the *k*s are rate constants. See ref 8 for discussion.

The third column of Table 1 lists the diagnostic ^{13}C chemical shifts of an MCP model compound, *n*-decylcyclopentane (see Figure 4 for nomenclature). These shifts agree satisfactorily with the predictions in column 2, which were made by using the published shifts of ethylcyclopentane[27] and temperature-corrected Grant−Paul parameters.[15] With recourse to the shifts of the model, the MCP peaks were easily assigned in the spectra of our dechlorinated PVC specimens that were made at low concentrations of monomer.

In Figure 2B, the MCP-1, -3,4, -α, and -*β* resonances are identified explicitly. Although the MCP-*β* peak appears in this figure as a shoulder, it was well-resolved in other spectra whose line widths were narrower. In such spectra, the MCP-2,5 resonance (not shown here) also was sufficiently well-resolved to appear as a separate peak. This peak is near the $-CH_2CH_2Cl$ resonance[19] of partially reduced long-chain ends. The chemical shifts of all of the MCP polymer resonances (in column 4 of Table 1) agree well with those of the model compound, and the MCP assignments gain further support from the relative intensities of the MCP-1, -3,4, and -α signals in Figure 2B. Thus all of the NMR evidence is consistent with the presence of the MCP chain terminus.

Backbiting Effects on Transfer to Monomer. Our recent work has shown that the monomer transfer constant for the polymerization of VC is equal to the sum of two terms, $C_{M,HH}$ and $C_{M,aux}$, that relate to the donation of chlorine atoms to VC from *β*-chloro macroradicals.[8] At a given temperature, $C_{M,HH}$ is a true constant that pertains to transfer instigated by head-to-head VC emplacement.[8] In contrast, the "auxiliary" term, $C_{M,aux}$, is a function of monomer concentration, and it has to do with the chemistry illustrated in Figure 5, where R• represents all of the possible *β*-halo radicals formed by intermolecular H abstraction (rate constant k_h) and backbiting (rate constant k_b'').[8] The internal allylic (IA) structures obviously must include those resulting from backbites (**18** and **19**), whose total concentration will be designated here as [BA]. A steady-state kinetic analysis based on the mechanism of Figure 5 shows that the rate of formation of BA segments is given by eq 14. Division of this equation by eq 5 produces eq 15, where $\bar{\rho}_{BA}$ is the number of BA groups per polymerized monomer unit.

$$d[BA]/dt = k_b'' k_s [P^\bullet]/(k_a' + k_s) \qquad (14)$$

$$\bar{\rho}_{BA} = \frac{d[BA]/dt}{d[PVC]/dt} = \frac{k_b'' k_s}{k_p(k_a' + k_s)[VC]} \qquad (15)$$

In our previous investigation,[8] PVC double-bond contents found by ^1H NMR were used to determine the values of $C_{M,HH}$ and $C_{M,aux}$, and these values were found to be in very good agreement with those deduced independently from polymer molecular weights. However, when the latter approach was used, the backbiting route to the IA groups was not accounted for explicitly and was considered to be of minor importance.[8] That idea can now be tested rigorously with the aid of eq 16,

$$(\overline{DP})_n^{-1} \approx C_{M,HH} - \frac{k_h k_s}{k_p(k_a' + k_s)} + \frac{k_s(k_h A + k_b'')}{k_p(k_a' + k_s)[VC]} \qquad (16)$$

$$[PVC] + [VC] \approx A \qquad (17)$$

$$C_{M,HH} \approx \text{intercept} + \frac{\text{slope}}{A} - \frac{k_b'' k_s}{k_p(k_a' + k_s)A} \qquad (18)$$

which was derived in the earlier study.[8] In this equation, $(\overline{DP})_n$ is the number-average degree of polymerization, and *A* is an approximately constant term [±(2−5)%][8] that eq 17 defines.

Equation 16 shows that plots of $(\overline{DP})_n^{-1}$ vs $[VC]^{-1}$ should be linear, a result that actually was obtained.[8] Equation 18 relates directly to such plots and indicates that their slopes and intercepts can be used to determine $C_{M,HH}$ when the last term in eq 18 is either known or negligible. From eq 15 it follows that this term is equal to $\bar{\rho}_{BA}[VC]/A$. The complete spectrum shown partially in Figure 2B reveals an MCP concentration per monomer unit of $0.1_5 \times 10^{-3}$. Therefore, in this case, $\bar{\rho}_{BA}$ is at least 0.3×10^{-3}, and it could be as high as 0.4×10^{-3} if reduction without cyclization occurred to some extent, as expected.[21] For this 55 °C polymerization, particle coalescence caused [VC] to be less than the equilibrium value of 1.5 M (calculated in the way described elsewhere[8,28]), and *A* was ca. 20.4 M in the concentration range studied by us.[8] Hence, at 55 °C, the magnitude of the last term in eq 18 is less than $(0.4 \times 10^{-3})1.5/20.4$, or $<0.03 \times 10^{-3}$. This value is negligible in comparison with the sum of the other two terms, which is 0.8×10^{-3} when the data of Hjertberg and Sörvik[24] are used to construct the plot.[8] Thus the calculation of $C_{M,HH}$ from the first two terms in eq 18 leads to only a minor error.

The same conclusion emerges from the data for polymerization at 80 °C. For our polymer made at this temperature with the VC pressure at 59% of saturation (see above), the MCP concentration found by NMR, 0.2×10^{-3} per VC unit, implies a maximum $\bar{\rho}_{BA}$ concentration of 0.5×10^{-3}. The [VC] value was 1.9 M, and the value of *A* was ca. 19.6 M. Thus, at 80 °C, the magnitude of the last term in eq 18 is $(0.5 \times 10^{-3})1.9/19.6$, or 0.05×10^{-3}. However, the sum of the first two terms is 1.7×10^{-3} when the Hjertberg−Sörvik data[24] for 80 °C are plotted.[8]

The results of Hjertberg and Sörvik[24] were used previously to plot eq 16 for polymerizations that were conducted at 45, 55, 65, and 80 °C under constant VC pressures.[8] Values of $C_{M,HH}$ then were determined from the first two terms of eq 18 and found to be in good agreement with those derived from ^1H NMR measure-

Table 2. Comparison of $C_{M,aux}$ Values

polym temp, °C	P/P_o[a]	$C_{M,aux}$ by ^{1}H NMR[b]	$C_{M,aux}$ from $\bar{M}_n$ data[c]
80	1.00	0.6 ± 0.1	0.6 ± 0.1
80	0.59	1.55 ± 0.2	1.75 ± 0.2
55	0.92	0.2 ± 0.1	0.4 ± 0.1
55	0.77	0.5 ± 0.1	0.7 ± 0.1
55	0.59[d]	1.15 ± 0.2	1.1 ± 0.2

[a] (Actual VC pressure)/(saturation VC pressure). [b] Values of $C_{M,aux} \times 10^3$ from ref 8. [c] Values of $C_{M,aux} \times 10^3$ from eq 19. [d] $\bar{M}_n = 31.8 \times 10^3$;[8] polymer prepared at the equilibrium concentration of monomer.

ments.[8] Applying the same procedure to the data for three polymers prepared in the BFGoodrich laboratories at 55 °C,[8] we now have observed a similar outcome. The molecular weights of those three polymers lead to a $C_{M,HH}$ value of $(0.85 \pm 0.1) \times 10^{-3}$, whereas the ^{1}H NMR data[8] gave a value of $(0.95 \pm 0.1) \times 10^{-3}$.

Because the molecular weight of PVC is controlled almost exclusively by transfer to monomer,[2b,29] eq 19

$$(\overline{DP})_n^{-1} = C_{M,HH} + C_{M,aux} \qquad (19)$$

applies.[8] It can be used to calculate values of $C_{M,aux}$ from $C_{M,HH}$ values deduced from molecular weights. In Table 2, some $C_{M,aux}$ values found in this way are compared with those obtained by the ^{1}H NMR method. The $(\overline{DP})_n^{-1}$ values required by eq 19 were obtained from regression fits of the plots of eq 16 that were made with the 80 °C data of Hjertberg and Sörvik[24] and the 55 °C data for the last three entries that Table 2 contains ($R^2 = 0.96$). The tabulated sets of $C_{M,aux}$ values are in good agreement, a result that further accredits the use of eqs 16−19 to determine transfer constants.

Concluding Remarks

The backbiting reactions discussed in this paper are important for several reasons. All of them cause the formation of structures that should be thermally labile, and the backbite that leads to allyl chloride segments is involved intrinsically in chain transfer to the monomer. In typical commercial PVCs, the concentrations of the DEB and BA structures always will be low. Nevertheless, both structures and perhaps the DEB groups, in particular, should significantly reduce the thermal stabilities of PVC fractions that are produced at very high conversions. Two intriguing aspects of the scheme in Figure 1 are the high k_b'/k_b ratio and the apparent nonformation of structure EHB. Statistical calculations might rationalize these discoveries.

Experimental Section

Materials. Bromine (Aldrich or Fisher), triphenylphosphine (Aldrich), 3-undecanol (Wiley), dimethylformamide (DMF, Analytical Reagent grade, Mallinckrodt), bis(cyclopentadienyl)-zirconium dichloride (Acros), 1-decene (Acros), ethylmagnesium chloride (2.0 M solution in ether, Aldrich), sodium (Aldrich), anhydrous ether (Fisher or Mallinckrodt), magnesium turnings (Analytical Reagent grade, Mallinckrodt), 2-ethyl-1-hexanol (Aldrich), iodine (Aldrich), 9-heptadecanone (TCI), cyclohexane (Fisher), hydrogen (Air Products), palladium (5%) on carbon (Aldrich No. 20,568-0), lithium borohydride (2 M solution in THF, Acros), and *n*-decylcyclopentane (Wiley) were obtained from the indicated commercial suppliers. Tetrahydrofuran (THF, Mallinckrodt) was distilled from disodium benzophenone dianion under nitrogen. When necessary, other liquid materials were dried thoroughly over 4A molecular sieves (Fisher) before they were used in reactions that were moisture-sensitive. The synthesis of the PVC samples made at constant monomer pressures has been described elsewhere.[8] These polymers were reduced with tri-*n*-butyltin hydride by a standard two-stage method[7,30] involving the use of THF and *m*-xylene, respectively, as the first- and second-stage solvents.

Instrumental Analysis. Proton-decoupled ^{13}C NMR spectra were obtained at 125.77 MHz with a Bruker AMX500 spectrometer or at 75.57 MHz with a GE QE−300 instrument that also served to record the 300.52-MHz ^{1}H NMR spectra of low-molecular-weight materials. A 60° pulse angle and a pulse repetition time of 10 s were used for the 125.77-MHz ^{13}C spectra, which were acquired at 100 or 110 °C from 15−20% solutions (w/v) of the samples in 1,2,4-trichlorobenzene/*p*-dioxane-d_8 (ca. 4:1 v/v) containing hexamethyldisiloxane as an internal reference (δ 2.00 ppm vs Me_4Si). The ^{13}C spectra recorded at ambient temperature and all of the ^{1}H spectra were obtained from chloroform-*d* solutions and are referenced to internal Me_4Si (δ 0.00 ppm).

The GC/MS analyses were performed with a Hewlett-Packard apparatus (Model 5890/5971A) equipped with a fused-silica HP-1 capillary column [cross-linked methylsilicone, 12 m × 0.2 mm (i.d.)]. Helium was used as the carrier gas, and the column temperature was increased from 50 to 300 °C at a rate of 20 °C/min.

Model Compound Syntheses: General Comments. Except where noted otherwise, reactions were carried out under nitrogen with continuous stirring. Organic solutions were dried with anhydrous magnesium sulfate and concentrated on a rotary evaporator at 35 °C under aspirator vacuum. Fractional distillations were performed with an H. S. Martin spinning band micro still equipped with a Teflon band and having a maximum separation efficiency of 150 theoretical plates. No attempts were made to optimize yields, and these usually were not determined, as the main synthetic objective was simply to obtain enough material for spectroscopic characterization and/or use in a subsequent step.

3-Bromoundecane (6). Bromine (3.00 mL, 9.36 g, 58.6 mmol) was added dropwise to a solution of triphenylphosphine (16.73 g, 63.8 mmol) and 3-undecanol (12.00 mL, 9.95 g, 57.7 mmol) in DMF (100 mL). When the mixture had cooled to room temperature, it was extracted with 3 × 200 mL of ether, and the combined extracts were washed with 3 × 200 mL of a solution prepared from equal volumes of water and concentrated aqueous HCl. The ether solution then was washed with 3 × 150 mL of water, dried, concentrated, and fractionally distilled to obtain **6** (bp 74−76 °C at 0.15 Torr) in a purity of 94%, according to GC/MS analysis: *m/e* (relative intensity) 155 (58, $M^+ - Br$) and 57 (100). ^{1}H NMR: δ 0.88 (t, 3H, CH_3-11), 1.04 (t, 3H, CH_3-1), 1.1−1.7 [m, 12H, (CH_2)$_6$CH$_3$], 1.7−2.0 (m, 4H, CH_2CHBrCH_2), and 3.97 ppm (qnt, 1H, C*H*Br). ^{13}C NMR (75.57 MHz, ca. 25 °C): δ 12.08 (C-1), 31.94 (C-2), 60.34 (C-3), 38.90 (C-4), 27.71 (C-5), 29.18, 29.34, and 29.55 (C-6, -7, and -8; exact assignments uncertain), 32.24 (C-9), 22.73 (C-10), and 14.12 ppm (C-11).

1-Bromo-2-ethyldecane (7). In a glovebag under argon, bis(cyclopentadienyl)zirconium dichloride (0.49 g, 1.7 mmol) and 1-decene (6.31 mL, 4.67 g, 33 mmol) were introduced into a flame-dried flask. Ethylmagnesium chloride (2.0 M solution in ether, 50.0 mL, 100 mmol) was added under nitrogen, and the mixture was allowed to remain at room temperature for 12 h. After the mixture was cooled to −78 °C, bromine (6.90 mL, 21.5 g, 134 mmol) was introduced during 30 s, and the mixture was kept for 1 h at ambient temperature. It then was extracted with three 150-mL portions of ether. The combined extracts were concentrated and fractionally distilled to obtain a sample of **7** (bp 89−93 °C at 0.20 Torr) that was shown to be ca. 90−95% pure by ^{1}H NMR and GC/MS analysis: *m/e* (relative intensity) 250 (0.6, M^+), 248 (0.7, M^+), 169 (26, $M^+ - Br$), 165 (55, $M^+ - C_6H_{13}$), 163 (55, $M^+ - C_6H_{13}$), 137 (13, $M^+ - C_8H_{17}$), 135 (14, $M^+ - C_8H_{17}$), and 71 (100); ^{1}H NMR: δ 0.89 (t, 6H, 2CH_3), 1.0−1.6 [m, 16H, CHCH_2CH$_3$ and (CH_2)$_7$CH$_3$], 2.5−2.7 (m, 1H, C*H*CH$_2$Br), and 3.45 ppm (d, 2H, CH_2Br). ^{13}C NMR (75.57 MHz, ca. 25 °C): δ 38.85 (C-1), 41.13 (C-2), 31.99

(C-3), 26.70 (C-4), 29.39, 29.64, and 29.89 (C-5, -6, and -7; exact assignments uncertain), 32.28 (C-8), 22.75 (C-9), 14.15 (C-10), 25.23 (Et branch CH_2), and 10.90 ppm (Et branch CH_3).

9,11-Diethylnonadecane (8, the DiEt Model). Sodium (ca. 1.0 g, 43 mg-atom) was added to a solution of **6** (1.52 g, 6.46 mmol) and **7** (1.61 g, 6.46 mmol) in dry ether (50 mL), and the mixture was kept at room temperature for ca. 3 days. Unchanged sodium was destroyed by the careful addition of a slight excess of 2-propanol, and the mixture was diluted with additional ether (100 mL). It then was washed with water (3 × 200 mL), dried, concentrated, and subjected to short-path distillation in order to remove all materials with boiling points ≤50 °C at 5 Torr. Analysis by GC/MS indicated that the residue was a 41:32:27 mixture of **8**, **9**, and **10**, respectively, containing minor amounts of impurities. This conclusion was supported by the ^{1}H NMR spectrum, which consisted only of resonances at δ 0.7$_5$−1.0 (m, 12H, 4CH_3), 1.0−1.6 (m, 34H, 17CH_2), and 2.1−2.2 ppm (m, 2H, 2CHCH$_2$CH$_3$). The identities of **9** and **10** were confirmed by comparing their GC retention times (**9**, 9.4 min; **10**, 10.3 min), mass spectra, and diagnostic ^{13}C NMR shifts with those of the authentic specimens whose preparations are described below. Compound **8** (GC retention time, 9.8 min) also was identified conclusively from its distinctive ^{13}C NMR resonances (see Table 1) and its mass spectrum: *m/e* (relative intensity) 324 (0.4, M$^+$), 295 (85, M$^+$ − Et), 211 (42, M$^+$ − C$_8$H$_{17}$), 155 (16, M$^+$ − C$_{12}$H$_{25}$), 154 (28, M$^+$ − C$_{12}$H$_{26}$), and 57 (100). Under the conditions used to obtain the 125.77-MHz carbon spectrum, the chemical shifts of the nonspecific resonances of **8**, **9**, and **10** were 14.08 (C-1), 22.96 (C-2), 32.31 (C-3), 29.70 (C-4), and 30.03 ppm (C-5). The spectrum also displayed two C-6 peaks at 30.55 and 30.57 ppm, which are discussed in the main text.

9,10-Diethyloctadecane (9). Magnesium turnings (0.16 g, 6.6 mg-atom), **6** (1.50 g, 6.4 mmol), and anhydrous ether (50 mL) were heated under reflux overnight. A saturated aqueous solution of ammonium chloride (50 mL) and additional ether (100 mL) were added in succession; then the ether layer was separated, washed with 3 200-mL portions of water, dried, concentrated, and subjected to short-path distillation at 5 Torr in order to remove constituents boiling at ≤50 °C. Analysis by GC/MS showed that the residue was **9** in a purity of 98%: *m/e* (relative intensity) 310 (0.4, M$^+$), 281 (18, M$^+$ − Et), 197 (9, M$^+$ − C$_8$H$_{17}$), 155 (21, M$^+$ − C$_{11}$H$_{23}$), and 154 (100, M$^+$ − C$_{11}$H$_{24}$). ^{1}H NMR: δ 0.7$_5$−1.0 (m, 12H, 4CH_3), 1.0−1.6 (m, 32H, 16CH_2), and 2.1−2.2 ppm (m, 2H, 2CHCH$_2$CH$_3$). ^{13}C NMR (125.77 MHz, 100 °C): δ 14.05 (C-1), 22.91 (C-2), 32.24 (C-3), 29.64 (C-4), 29.96 (C-5), 30.49 (C-6), 28.62 (C-7), 31.38 and 31.41 (C-8), 42.71 and 42.73 (C-9), 24.26 (Et branch CH_2), and 12.79 ppm (Et branch CH_3).

9,12-Diethyleicosane (10). A coupling reaction of **7** (1.50 g, 6.0 mmol) was carried out with magnesium turnings (0.15 g, 6.2 mg-atom) in dry ether (50 mL) according to the procedure used to synthesize **9**. An analogous workup and distillation afforded residual **10** in a purity of 97%, according to GC/MS and ^{1}H NMR analysis: *m/e* (relative intensity) 338 (0.1, M$^+$), 309 (12, M$^+$ − Et), 225 (5, M$^+$ − C$_8$H$_{17}$), 155 (5, M$^+$ − C$_{13}$H$_{27}$), 154 (11, M$^+$ − C$_{13}$H$_{28}$), and 57 (100); ^{1}H NMR: δ 0.7$_5$−1.0 (m, 12H, 4CH_3), 1.0−1.8 (m, 36H, 18CH_2), and 2.4−2.7 ppm (m, 2H, 2CHCH$_2$CH$_3$); ^{13}C NMR (125.77 MHz, 100 °C): δ 14.05 (C-1), 22.92 (C-2), 32.25 (C-3), 29.64 (C-4), 29.99 (C-5), 30.51 (C-6), 27.38 (C-7), 34.11 (C-8), 40.19 (C-9), 31.14 (C-10), 26.82 (Et branch CH_2), and 11.22 ppm (Et branch CH_3).

1-Bromo-2-ethylhexane (11). To a solution of 2-ethyl-1-hexanol (15.6 mL, 13.0 g, 100 mmol) and triphenylphosphine (28.1 g, 107 mmol) in DMF (100 mL), bromine was added dropwise until 2 drops caused the solution to acquire a permanent orange coloration. The resulting exothermic reaction raised the temperature of the mixture to 55 °C. After the mixture had cooled to room temperature, it was extracted with 3 × 200 mL of ether, and the combined extracts were washed with 3 × 200 mL of a solution prepared from equal volumes of water and concentrated aqueous HCl. The organic moiety then was washed with 3 × 300 mL of water, dried, concentrated, and fractionally distilled to obtain 17.6 g (yield, 91%) of **11** (bp 31−35 °C at 0.10 Torr) in a purity of 99%, according to GC/MS analysis: *m/e* (relative intensity) 194 (0.9, M$^+$), 192 (1.0, M$^+$), 165 (7, M$^+$ − Et), 163 (7, M$^+$ − Et), 137 (5, M$^+$ − Bu), 135 (5, M$^+$ − Bu), 113 (13, M$^+$ − Br), and 57 (100). ^{1}H NMR: δ 0.95 and 0.93 (overlapping t's, 6H, 2CH_3), 1.1$_5$−1.6$_5$ [m, 9H, CH$_3$CH_2CH(CH_2)$_3$], and 3.48 ppm (d, 2H, CH_2Br). ^{13}C NMR (75.57 MHz, ca. 25 °C): δ 38.67 (C-1), 41.50 (C-2), 32.16 (C-3), 29.06 (C-4), 22.96 (C-5), 13.99 (C-6), 25.46 (Et branch CH_2), and 10.90 ppm (Et branch CH_3).

9-(2-Ethyl-*n*-hexyl)-8-heptadecene (13) and 5-Ethyl-7-*n*-octyl-6-pentadecene (14). In a flame-dried flask, a solution of **11** (12.64 g, 65.4 mmol) in anhydrous ether (100 mL) was added slowly to a mixture of anhydrous ether (300 mL), magnesium turnings (1.59 g, 65.4 mg-atom), and two small iodine crystals. The mixture was heated under reflux until the iodine color disappeared and then was allowed to stand at ambient temperature overnight. Following the slow introduction of a solution of 9-heptadecanone (4.00 g, 15.7 mmol) in dry ether (50 mL), the reaction was allowed to continue at autogenous temperature for 3 h and subsequently was terminated by adding a saturated aqueous solution of ammonium chloride (50 mL). The ether layer was separated, and the aqueous moiety was extracted with 3 × 150 mL of ether. All of the ethereal fractions then were combined, dried, and freed of ether by rotary evaporation. Analysis by GC/MS of the residue thus obtained revealed that the major constituent with the longest retention time (11.3 min) produced a very intense mass spectral peak (relative intensity, 100) at *m/e* 255. This value corresponds to the (M$^+$ − C$_8$H$_{17}$) ion expected to result from alcohol **12**.

Materials boiling up to 136 °C (final pot temperature, 198 °C) were removed from the residue by fractional distillation at 0.10 Torr. This operation caused the quantitative destruction of **12** and left undistilled a residue that consisted of unchanged ketone, some minor byproducts, and two major products whose area ratio was 35:65. The latter materials had GC retention times of 10.5 min (product 1) and 10.6 min (product 2), respectively, and they were identified tentatively as **13** and **14** on the basis of their mass spectra: product 1 (**14**?), *m/e* (relative intensity) 350 (21, M$^+$), 321 (69, M$^+$ − Et), 293 (63, M$^+$ − Bu), 253 (4, M$^+$ − C$_7$H$_{13}$), and 237 (100, M$^+$ − C$_8$H$_{17}$); product 2 (**13**?), *m/e* (relative intensity) 350 (39, M$^+$), 321 (14, M$^+$ − Et), 293 (12, M$^+$ − Bu), 253 (49, M$^+$ − C$_7$H$_{13}$), 252 (33, M$^+$ − C$_7$H$_{14}$), 237 (35, M$^+$ − C$_8$H$_{17}$), and 139 (100).

9-(2-Ethyl-*n*-hexyl)heptadecane (15, the EtHe Model). A 3.47-g portion of the mixture thought to incorporate **13** and **14** was dissolved in cyclohexane (80 mL) and subjected to catalytic hydrogenation at ambient temperature in the presence of 1.0 g of a Pd(5%)/C catalyst. The reaction was carried out for 6 h with constant shaking under a hydrogen pressure of 4 atm. Filtration and subsequent rotary evaporation of the filtrate gave a residue that was shown by GC/MS analysis to consist of **15**, 9-heptadecanone, 9-heptadecanol (**16**), and minor impurities in an area ratio of ca. 70:15:10:5, respectively. The starting ketone and alcohol **16** were identified by comparing their GC retention times and mass spectra with those of authentic specimens, and the distinctive resonances of these compounds were assigned easily in the ^{13}C NMR spectrum of the mixture, which was obtained at 125.77 MHz and 100 °C. In that spectrum, the diagnostic peaks of **16** were those for C-7, -8, and -9 (see below), while the diagnostic resonances of the ketone appeared at δ 24.34 (C-7), 42.85 (C-8), and 208.20 ppm (C-9). The structure of **15** was established by the characteristic carbon resonances given in Table 1 and by the mass spectrum of the compound, as obtained from GC/MS analysis: *m/e* (relative intensity) 352 (1, M$^+$), 323 (20, M$^+$ − Et), 295 (11, M$^+$ − Bu), 239 (100, M$^+$ − C$_8$H$_{17}$), and 238 (53, M$^+$ − C$_8$H$_{18}$).

9-Heptadecanol (16). A 2 M solution of lithium borohydride in THF (10 mL, 20 mmol) was added during 1 h to a solution of 9-heptadecanone (3.00 g, 11.8 mmol) in dry THF (20 mL) while the temperature was kept near 0 °C by external cooling. After 3 h of reaction at 0−5 °C, methanol (5 mL) was introduced over 20 min while cooling was continued, and the mixture was kept at room temperature for an additional 3 h. Dilution with ether (50 mL), followed by washing with water

(3 × 200 mL), drying, and concentration left a residue whose major constituent (88 area %) was identified as **16** by GC/MS analysis: *m/e* (relative intensity) 256 (0.1, M^+), 238 (9, $M^+ - H_2O$), and 143 (100, $M^+ - C_8H_{17}$). ^{1}H NMR: δ 0.88 (t, 6H, $2CH_3$), 1.0−1.6 (m, 28H, $14CH_2$), and 3.5−3.6$_5$ ppm (m, 1H, CHOH). ^{13}C NMR (125.77 MHz, 100 °C): δ 14.05 (C-1), 22.92 (C-2), 32.24 (C-3), 29.60 (C-4), 29.98 and 30.20 (C-5 and -6, exact assignments uncertain), 26.09 (C-7), 38.26 (C-8), and 71.91 ppm (C-9).

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