Oligomerization of Vinyl Monomers. 9. ^{13}C NMR and Chromatographic Studies of Oligomers of 2-Vinylpyridine[1]

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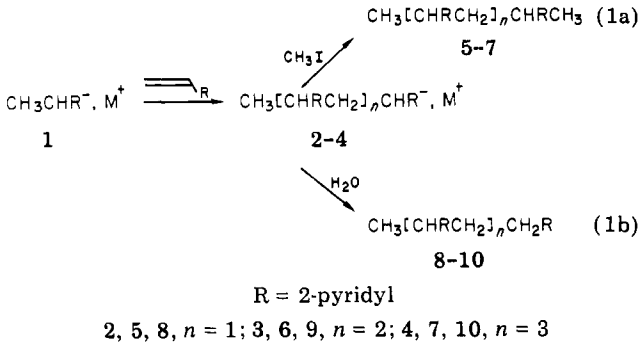
ABSTRACT: Dimeric, trimeric, and tetrameric anions formed by addition of 2-vinylpyridine to lithio and potassio salts of 2-ethylpyridine in THF at −78 °C were terminated with $^{13}CH_3I$ and with H_2O and were analyzed by analytical high-pressure liquid chromatography, capillary gas chromatography, and ^{13}C NMR. The three techniques show very good agreement and provide complementary information on the stereochemistry of monomer addition and methylation. The six stereoisomers of the methylated tetramer were identified by partially and completely isomerizing an isotactic sample with *t*-BuOK/Me_2SO and analyzing by GC. In contrast to previous findings, the addition of 2-vinylpyridine in the presence of Li ion is only moderately isotactic-like (~60%). However, in agreement with previous results, the methylation is highly (>99%) stereoselective regardless of the degree of oligomerization. In the presence of K^+ ion, neither methylation nor monomer addition is highly stereoselective. The dramatic difference in the degree of stereoselectivity between methylation and monomer addition in the presence of Li^+ was rationalized by considering the role of intramolecular chelation in the development of the transition state for the 2-vinylpyridine addition reaction.

Introduction

Recently we reported on the stereochemistry of anionic oligomerization of 2- and 4-vinylpyridines in THF[3-5] and concluded that the apparent stereoselectivity observed in the oligomerization–methylation sequence (eq 1a) of 2-



R = 2-pyridyl

2, 5, 8, n = 1; 3, 6, 9, n = 2; 4, 7, 10, n = 3

vinylpyridine is due to an intramolecular chelation of the alkali metal cation and the nitrogen lone pair of the penultimate pyridine ring (Figure 1). Such a coordination process renders the chain end conformationally rigid and leads to a preference of ion pair **11** over its diastereomer **12**. Such a model correctly predicts the lack of methylation stereoselectivity observed for the 1,3-di(4-pyridyl)butane anion and accounts for the decrease in methylation stereoselectivity observed with larger and more extensively coordinated cations. The detailed stereochemistry of vinyl addition in the presence of larger and more extensively coordinated cations could not be examined due to the larger number of stereoisomers generated and the presumed presence of as yet unidentified side products.

We have recently found that these compounds (**5–10**) may be conveniently analyzed by capillary gas chromatography. This constitutes a considerable advantage since it not only allows a rapid, convenient, and accurate determination of stereoisomers **5–7** but also facilitates an evaluation of the stereochemistry of formation of products **8–10**. Hence the stereochemistry of methylation and of monomer addition may be independently evaluated. The availability of medium-pressure preparative liquid chromatography, moreover, has provided us with a greater preparative capability so that these previously unresolved problems could be examined. We now wish to confirm that, as observed previously, in the presence of small cations such as Li, the methylation of anions **2–4** is highly stereoselective. However, the addition of 2-vinylpyridine to these lithio salts, although predominantly isotactic-like, is not and appreciable quantities of heterotactic-like isomers are formed. It also appears that the stereochemistry of 2-vinylpyridine addition under these conditions is dependent upon chain length for the first few additions.

Results

The 2-vinylpyridine oligomeric anions were prepared as described previously and were both methylated and protonated (H_2O) in order to separately determine the stereochemistry of methylation and of monomer addition (eq 1). The crude methylation product was isolated as previously described and was separated on a Merck Lobar silica gel column by solvent gradient medium-pressure preparative liquid chromatography using hexane and CH_2Cl_2/CH_3OH (4/1) (see Experimental Section).[6,7] The liquid chromatogram indicates an excellent base line separation up to pentamers and beyond. The products were identified by ^1H and ^{13}C NMR, by analytical high-pressure liquid chromatography, and by capillary gas chromatography.

Dimer–Trimer Stereochemistry. The results obtained for the dimers (**5**) and the trimers (**6** and **9**) prepared in the presence of Li and K counterions are shown in Table I and Figure 2.[8] The stereochemical assignments were facilitated by the previous characterization of the corresponding isotactic products, principally by ^1H NMR of the methylene and the CH_3 end groups. In the present case, the stereochemistry of the products was also evaluated by ^{13}C NMR of the product terminated by 25%-enriched $^{13}CH_3I$.[9] This simplifies the stereochemical analysis and is, moreover, useful when correlating trimer stereochemistry with that of higher oligomers and polymers for which the ^{13}C signal of the unlabeled methyl end group tends to be too weak for convenient analysis. The assignments for the racemic dimer, (r), and the heterotactic, (mr), and syndiotactic, (rr), trimers were aided by the epimerization of the products. Since the two methyl groups in a heterotactic trimer are nonequivalent, we expect to see a possible total of four $^{13}CH_3$ NMR absorptions. This is the case for the trimer (**6**) formed in the presence of K ion [**6** (K)]. Table I shows the very good agreement between the four methods employed. The GC analysis is particularly useful since it allows a convenient and rapid analysis of the stereoisomers of a particular oligomer without the need for a prior separation of products. For instance, we were able to show that the relative proportions of stereoisomers in dimer, trimer, and tetramer were the

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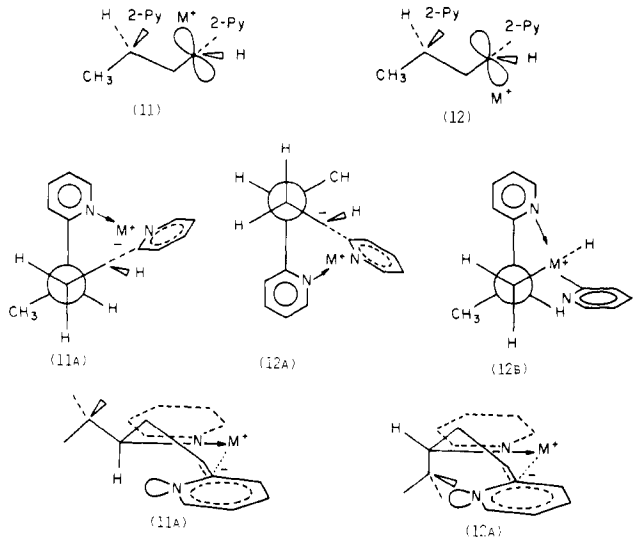


Figure 1. Intramolecular chelation as a factor in the equilibrium between ion pair diastereomers 11 and 12.

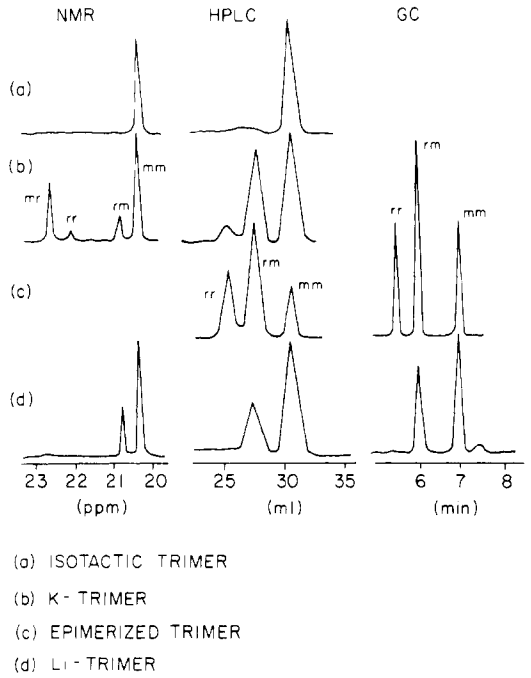


Figure 2. HPLC, GC, and ^{13}C NMR of the trimer 6 prepared in the presence of Li and K ions in THF at −78 °C.

same in the isolated fractions as in the crude reaction product. Thus there appears to be no partial overlap between the first three oligomers in the liquid chromatogram, and the results for the higher oligomers likewise indicate an absence of such complications.[10] The data show, moreover, that, in contrast to previous results, the formation of trimer according to eq 1 in the presence of Li as counterion is only slightly stereoselective. However, only the (mm) and (mr) [or (rm)] stereoisomers are formed. Hence either the methylation or the monomer addition is stereoselective. Analysis by GC of the protonated trimer (Li) **9** (eq 1b) shows the presence of two peaks in the approximate ratio of 2:3. This ratio is about the same as that obtained by methylation, so it is the monomer addition step that is not stereoselective. Comparison with the corresponding ^{13}C NMR spectrum of the ^{13}C-labeled CH_3 end group indicates then that the first peak downfield from the (mm) absorption is (rm). Comparison of the GC (LC) chromatograms and the ^{13}C NMR spectrum of the

Table I
Comparison of NMR and Chromatographic Data for Fractions of Stereoisomers in Dimers 5 and Trimers 6 and 9 Prepared in the Presence of Li and K Ions[a] in THF at −78 °C

		60-MHz ^1H NMR	25-MHz ^{13}C NMR	GC[c]	HPLC[d]
		Dimers			
5 (Li)	(m)	1.00	0.98	0.99	
	(r)	~0	0.02	0.01	
5 (K)	(m)	0.85	0.87	0.86	
	(r)	0.15	0.13	0.14	
5 (epimerized)	(m)			0.49	
	(r)			0.51	
		Trimers			
6 (Li)	(mm)		0.65	0.64	0.64
	(mr)		~0	} 0.36	} 0.36
	(rm)		0.35		
	(rr)		~0	~0	~0
6 (K)	(mm)		0.48	0.49	0.50
	(mr)		0.32	} 0.45	} 0.43
	(rm)		0.12		
	(rr)		0.08	0.06	0.07
6 (epimerized)	(mm)	~0.25[b]		0.23	0.24
	(mr)	~0.55[b]		} 0.50	} 0.46
	(rm)	~0.20[b]			
	(rr)			0.27	0.29
9 (Li)	(m)			0.63	
	(r)			0.37	
9 (epimerized)	(m)			0.47	
	(r)			0.53	

[a] Initiator concentrations ~10^{-1} M. The effect of initiator concentration has been examined in the 10^{-1}-10^{-3} M range (see text). [b] Reference 3a. [c] Dimethylsilicone-coated, 12-m glass capillary column. Injector, oven, and detector temperatures: 250, 210, and 250 °C, respectively. [d] Column: 25-cm, 5-μm Ultrasphere Si (Altex). Solvent: isooctane (50), CH_2Cl_2 (9), CH_3OH (1); 0.01% of triethylammonium acetate added.

trimer (K) completes the NMR assignments of the $^{13}CH_3$ end group as (mr), (rr), (rm), and (mm) from low to high field. Table I indicates that for the formation of trimer (K) neither the methylation nor the vinyl addition is highly stereoselective, consistent with earlier qualitative findings.[3a] Thus for both Li and K systems, the methylation stereochemistry of dimer and trimer anion is similar (see below).

Tetramer Stereochemistry. The stereochemistry of formation of tetramer **7**, according to eq 1, is more complex than that of trimer since six stereoisomers may be formed: the symmetrical oligomers (mmm), (mrm), (rmr), and (rrr) and the unsymmetrical stereoisomers (mmr) and (rrm). For the $^{13}CH_3I$-terminated tetramer, moreover, the (mmr) and (rmm) as well as the (rrm) and (mrr) ^{13}C NMR absorptions are expected to be different. The GC chromatograms of an isotactic tetramer (prepared by careful preparative liquid chromatography), a partially and a completely epimerized (*t*-BuOK/Me_2SO) isotactic tetramer, and the tetramers prepared in the presence of Li and K ions are shown in Figure 3. The results are tabulated in Table II.

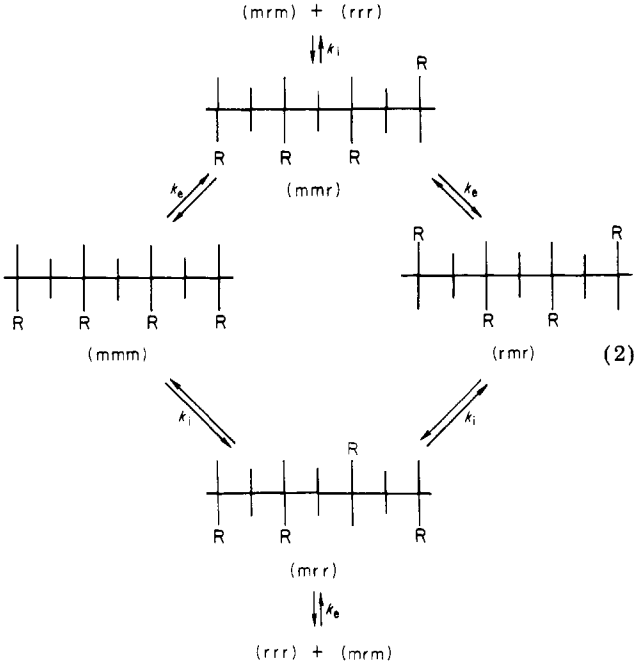
The complete epimerization suggests that components 3 and 4 pertain to the unsymmetrical oligomers (mmr) and (rrm). Partial epimerization of the isotactic tetramer (30 min at room temperature) surprisingly produced only component 4 along with an appreciable quantity of component 2 (Figure 3). Components 1, 3, and 5 are formed at a much slower rate, and epimerization at room temperature generally takes up to 300 h for completion. This indicates that the epimerization of the external (k_e) and

Table II
Stereoisomers of 7 and 10 Prepared[a] in the Presence of Li and K Ions and the Corresponding Partially[b] and Completely Epimerized[c] Isotactic 7 Determined by ^{13}C NMR and GC[d]

	7 (Li)		7 (epimerized) GC		7 (K)		
	GC	^{13}C NMR	compl[b]	part[c]	GC	^{13}C NMR	10 (Li) GC
(mmm)	0.57	0.59	0.09	0.66	0.48	0.49	0.54 (mm)
(mrm)	0.25	0.21	0.13		0.20	0.21	0.29 (mr)
(mmr)	0.10		0.25	0.28	0.15	0.09	0.10 (rm)
(rmm)		0.11				0.06	0.07 (rr)
(mrr)	0.08		0.25		0.14	0.08	
(rrm)		0.09				0.04	
(rmr)			0.14	0.06	0.014	0.03	
(rrr)			0.14		0.013		

[a] At −78 °C in THF. Initiator concentration ~10^{-1} M. [b] Epimerized at 25 °C in *t*-BuOK/Me_2SO for 10 min. [c] Epimerized at 25 °C in *t*-BuOK/Me_2SO for about 300 h. [d] Dimethylsilicone-coated, 12-m capillary column. Injector, oven, and detector temperatures: 250, 245, and 300 °C, respectively.

internal (k_i) asymmetric carbons proceeds at greatly different rates. Thus according to eq 2, if the external carbon is preferentially epimerized, isomer (mmr) would be formed first followed by (rmr). The preferential isomerization of the internal carbon would lead to (mmm) → (mrr) → (rmr).



In order to resolve this question, isotactic trimer (mm) was partially epimerized under the same conditions. Partial epimerization (~5 min) produced about 11% of (mr) [or (rm)] and only 0.34% of (rr). This demonstrates the much faster epimerization of the external asymmetric center, so $k_e \gg k_i$. Assuming that the rate of epimerization of external carbon is the same for (mm) and (mr) stereoisomers, the data can be accommodated with a k_e/k_i ratio greater than 60. The kinetics of epimerization of isotactic tetramer is shown in Figure 4. Over a period of ~5 h, only two stereoisomers are generated, and the composition of the mixture approaches an (mmm)/(mmr)/(rmr) ratio of 1/2/1. The above observations allow us to assign all tetramer peaks except 1 and 5. Given the observed general correlation between retention time and meso content, these two peaks are assigned as (rrr) and (mrm), respectively (see below). Figure 3 also shows the gas chromatograms of the methylated tetramer prepared in the presence of Li and K ions. Tetramer prepared in the presence of Li ion (tetramer (Li)) shows only four peaks (3, 4, 5, and 6), while tetramer prepared in the presence of K ion (tetramer (K)) appears to contain all six stereoisomers (Table II). Apparently, only the (rrm), (rmm), (mrm), and (mmm) stereoisomers are generated in the presence of Li ion so the methylation appears to be highly stereoselective as ob-

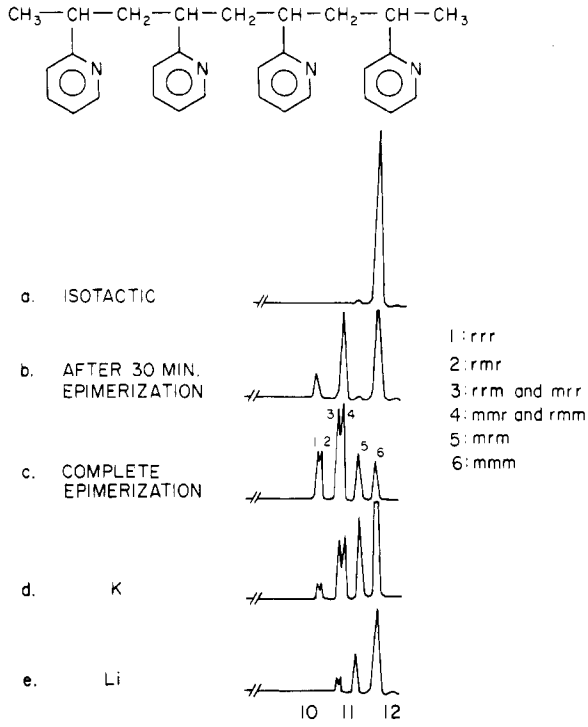


Figure 3. Gas chromatograms of isotactic tetramer (7), partially and completely epimerized isotactic 7, and the tetramers 7 prepared in the presence of Li and K ions at −78 °C in THF.

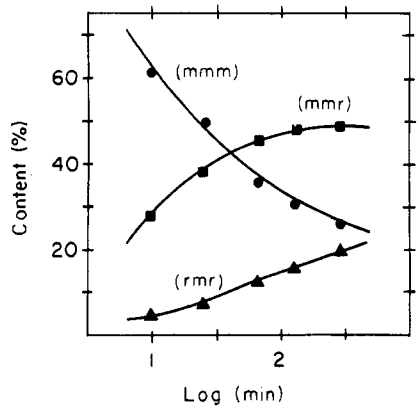


Figure 4. Kinetics of epimerization of isotactic tetramer 7 in *t*-BuOK/Me_2SO at 25 °C: (●) (mmm); (■) (mmr); (▲) (rmr).

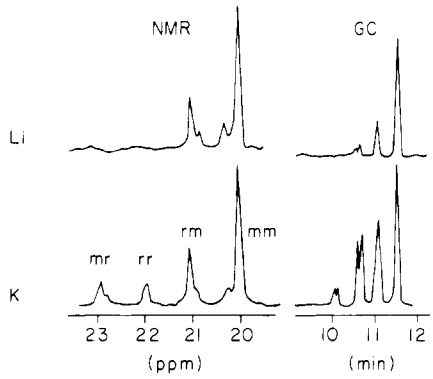


Figure 5. ^{13}C NMR spectra of the terminal $^{13}CH_3$ group of tetramer 7 prepared in the presence of Li and K ions in THF at −78 °C.

served for the trimer. The corresponding protonated tetramer, as expected, shows four GC peaks in the same ratio as the corresponding methylated sample. These peaks, in order of increasing retention time, should thus be (rr), (rm), (mr), and (mm).

The ^{13}C NMR spectra of the tetramer prepared in the presence of Li and K ions and terminated with $^{13}CH_3I$ (25% enriched) are shown in Figure 5.

Two main absorptions previously assigned as due to (mm) and (rm) are observed for tetramer (Li), but fine structure due to the additional asymmetric center can be observed. The demonstration of the (rm) signal and the quantitative correlation with the GC data (Table III) confirms the assignment of GC peak 5 as (mrm) (see above). Tetramer (K) shows all four groups of $^{13}CH_3$ signals. Correlation with the corresponding gas chromatograms (Figure 5) allows convenient assignment of all seven peaks observed for tetramer (K) in order of increasing field as (mmr), (rmr), (rrr) + (mrr), (mrm), (rrm), (rmm), and (mmm). Evaluation of the relative proportions of the stereoisomers is shown in Table II and indicates excellent agreement with the GC data. As observed in the case of the trimer, the addition of monomer to the lithio salt of the trimer anion is not highly stereoselective. A similar conclusion may be drawn for the corresponding monomer addition to the potassium salt.

The lack of stereoselectivity in the addition of monomer to oligomeric anions is puzzling in view of the observed very high methylation stereoselectivity. This perhaps could be influenced by variables such as carbanion purity, concentration, and other conditions such as the presence of residual *n*-BuLi used in the preparation of lithio-2-ethylpyridine or of 2-ethylpyridine. The effects of these variables are reported in Table III. The results show no effects from the presence of unreacted *n*-BuLi or 2-ethylpyridine on the stereoisomer distribution. However, a small but reproducible effect of carbanion concentration on the stereochemistry of formation of dimer **5** and tetramers **7** and **10** is present. Thus a small increase in methylation stereoselectivity and a decrease in monomer addition stereoselectivity is observed with a 100-fold decrease in initiator concentration. The stereochemistry of trimer formation is not affected, perhaps as a result of canceling effects. The reason for these variations is not clear at present but may be related to the presence of triple ions at higher concentrations.[11,12] However, the effects are relatively small and indicate that the lack of stereoselectivity in the addition of monomer is not caused by the above factors. The effect of [monomer]/[initiator] ratio was also briefly investigated. Thus, the protonated trimer **9** was prepared using ratios varying from 0.8 to 10. The (m)/(r) ratio of the product (~1.5) determined by HPLC did not vary up until a ratio of 5; but at a ratio of 10 the (m)/(r) ratio of the product increased to about 3, presumably as a result of a faster depletion of the racemic trimer anion.

Table III
Stereochemistry of Formation of Products 5-10 (%) in the Presence of Li Ion as a Function of Initiator Purity, Concentration, and *n*-BuLi/2-Ethylpyridine Ratio Determined by GC[a]

	$M \times 10^{-3}$ [b]						
[initiator]	300	200[c]	100[d]	100[e]	50	2.3	1.3
5 (r)	1.5	1.5	0.7	0.4	0.5	0.2	0.2
(m)	98.5	98.5	99.3	99.6	99.5	99.8	99.8
9 (r)		38.5	38.5	36.2	37.2		
(m)		61.5	61.5	63.8	62.8		
6 (rr)	1.0	1.5	0.9	0.5	2.3	0.3	0.4
(mr)	43.0	40.3	41.0	42.0	38.0	41.2	42.2
(mm)	56.0	58.2	58.1	57.5	59.7	58.5	57.4
10 (rr)		4.2	1.3	1.5	6.8		
(rm)		4.8	1.6	2.5	10.0		
(mr)		32.0	33.7	33.5	29.5		
(mm)		59.0	63.4	62.5	53.7		
7 (rrr)							
(rmr)		0.3		0.1			0.4
(rrm)	1.9	4.6	3.3	3.2	8.3	11.6	11.0
(mmr)	3.4	5.8	3.7	4.3	10.9	12.0	10.5
(mrm)	31.6	34.1	32.3	32.0	28.4	28.8	29.8
(mmm)	63.4	55.2	60.7	60.4	52.4	47.6	48.3

[a] For conditions, see Tables I and II. [b] Approximate concentrations. [c] The lithio salt of 2-ethylpyridine was recrystallized. [d] [*n*-BuLi]/[2-ethylpyridine] was 0.3. [e] [*n*-BuLi]/[2-ethylpyridine] was 3.0.

Discussion

In agreement with previous findings, the methylation of the dimeric and trimeric anions in the presence of Li ions proceeds in a highly stereoregular fashion (>99%). In contrast to previous findings, however, the corresponding addition of 2-vinylpyridine, although predominantly isotactic-like, is not (~63%). The reason for the discrepancy is the rather crude separation method (gravity liquid chromatography) previously employed that apparently did not result in a clear separation between meso dimer and heterotactic trimer. The resulting imperfect integration of the corresponding trimer fraction and the complexity of its NMR spectrum caused us to misinterpret the spectrum of the heterotactic trimer as due to a "side product". The newer techniques employed, especially capillary GC, clearly show the absence of any major unidentified low molecular weight compounds. Moreover, the gas chromatograms of the oligomers present in the crude product and the fractions isolated by LC are identical, so the LC separation itself does not lead to distortions in the distribution of stereoisomers. For the oligomerization in the presence of K^+ ion, the formation of dimer is actually somewhat more meso selective than previously determined (85 vs. 63%). The reason for this is most likely that the previous method involved a distillation of the dimer from the reaction mixture. Since, according to our GC data, the racemic isomer is somewhat more volatile than the meso isomer, the distillation is expected to lead to a relative enrichment of the distillate in the racemic stereoisomer. The formation of trimer (K) clearly indicates that the vinyl addition is not highly stereoselective. This is not unexpected since the methylation is not stereoselective either.

The availability of the ^{13}C NMR data allows a quantitative evaluation of the methylation stereochemistry of the dimer, trimer, and tetramer anions and that of the 2-

Table IV
Stereochemistry of Formation of Last and Next-to-Last Dyads in Oligomers Prepared in the Presence of Li and K Ions in THF at −78 °C

	dimer (5)	trimer (6)	tetramer (7)
$P_{m,1}$			
Li	⩾0.99	⩾0.99	⩾0.99
K	0.87	0.60	0.80
$P_{m,2}$			
Li		0.65 (0.63)[b]	0.70 (0.64)[c]
K		0.80	0.65

[a] Calculated according to eq 3. [b] Calculated from the GC data (Table I) for protonated trimer 9. [c] Calculated from the GC data on the protonated tetramer 10 (Table II).

vinylpyridine addition to the dimeric and trimeric anions.

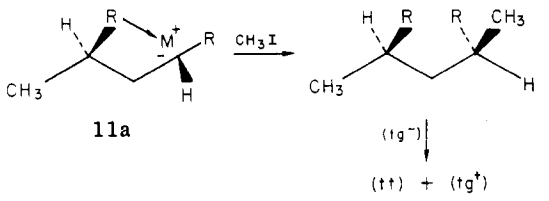
The probability of a meso placement in the last dyad and next to last dyad of an oligomer ($P_{m,1}$ and $P_{m,2}$, respectively) are given by

$$P_{m,1} = \frac{(mm) + (rm)}{(mm) + (rm) + (mr) + (rr)}$$

$$P_{m,2} = \frac{(mm) + (mr)}{(mm) + (rm) + (mr) + (rr)} \quad (3)$$

The results are tabulated in Table IV. As pointed out, the methylation in the presence of Li ion is highly stereoselective regardless of the degree of oligomerization. The methylation in the presence of K^+ ion is not and, moreover, shows a considerable variation with the degree of oligomerization. This indicates that effects of antepenultimate and/or prior asymmetric carbon atoms may be present (see below).

The difference in stereoselectivity of the lithium salt of the dimeric anion toward CH_3I and 2-vinylpyridine is puzzling. The methylation stereoselectivity is very high indeed and clearly points to a conformationally restrained oligomeric anion in which the metal ion is coordinated with the nitrogen lone pair of the penultimate pyridine ring. The lack of stereoselectivity of the monomer addition reaction, however, is surprising, and it may be postulated that this is due to the greater steric bulk of the monomer compared to methyl iodide. Thus, cation side reaction of **11a** with CH_3I is expected to lead immediately after reaction to the unfavorable tg^- conformation of the pentane dimer (eq 4),[13] and the corresponding monomer addition



11a (4)

process may be expected to result in greater steric stress in the transition state. However, the difference is not expected to be great enough to account for the very substantial difference in stereoselectivity (3/2 vs. 99/1). A more plausible explanation is based upon electronic factors.

Figure 6 shows a description consistent with the observations. The monomer adds to the energetically preferred (*Z*)-**11a** anion[4] and immediately upon addition yields (*Z*)-**11a′**, in which the intramolecular chelation is absent. Since, according to our previous results, this chelation is strongly favored, its absence in (*Z*)-**11a′** is expected to render this pathway less attractive. The corresponding reaction of (*E*)-**11a** would not have this

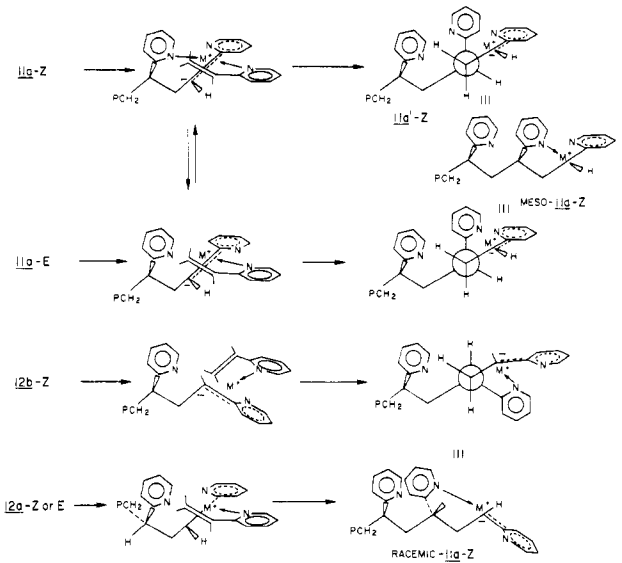


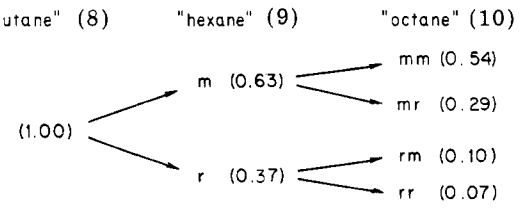
Figure 6. Possible modes of reaction with monomer of the *E* or *Z* forms of anions **11** or **12**.

problem, but this isomer should be less stable than (*Z*)-**11a** since the distance between metal ion and the nitrogen atom of the carbanion pyridine is greater. As a result, a third or fourth pathway (Figure 6) in which monomer addition to (*Z*)-**12b** or (*Z*)-**12a**, respectively, leads to a racemic-like placement may compete with the alternate pathways described above. Another possibility for a racemic-like addition would be the reaction of (*Z*)-**11a** or (*E*)-**11a** with monomer approaching the anion from the side opposite the metal ion (anti). This pathway seems less attractive because of the formation of an energetically unfavorable product-separated ion pair.[3a] Moreover, the availability of such a pathway would be inconsistent with the high stereoselectivity observed for the corresponding methylation reaction. Following this description, the monomer addition then is not stereoselective due to the requirement that the newly formed anion is intramolecularly chelated. Thus the same factor (intramolecular chelation) that is responsible for the very high methylation stereoselectivity prevents the stereoselective addition of 2-vinylpyridine. The above-proposed mechanism would lead to the prediction that the addition to anion **2** of 4-vinylpyridine (and similar electrophiles), for which intramolecular chelation by penultimate 2-pyridine has been shown to be absent, should be stereoselective. Experiments along these lines are in progress.

The stereochemistry of methylation and 2-vinylpyridine addition to the K salts of the oligomeric anions **2**–**4** is consistent with the mechanism previously proposed. Thus the preferred chelated form (**11a**) of the anions should be in equilibrium with an unchelated conformer for which no stereoselectivity is expected upon reaction with either CH_3I or 2-vinylpyridine.

The observation that the addition of 2-vinylpyridine in THF at low temperature in the presence of Li ions is not stereoregular resolves some previously unexplained findings.[14] Thus termination with ^{13}C-labeled CH_3I of a low molecular weight (DP ≃ 60) "living" polymers prepared in THF in the presence of Li^+ produced a polymer showing a distinct $^{13}CH_3$ doublet absorption, the origin of which was unclear. The present results clearly point to the two absorptions as being due to the (rm) and (mm) groups of stereoisomers. Likewise, the relatively sharp methyl doublets observed for the pentamer–hexamer mixture were incorrectly interpreted as due to a very highly stereoregular

Scheme I
Relative Proportions of Stereoisomers of 9 and 10



polymerization process. Due to the very highly stereoselective methylation, the (rm) and (mm) CH_3 NMR absorptions could not be resolved. Studies on these higher oligomers are being completed and will be reported in the near future.

A comparison of the relative proportions of stereoisomers (Li) of the protonated trimer and tetramer (Scheme I) indicates that the stereochemistry of vinyl addition leading to the formation of these oligomers is complex. Thus the total racemic content in the first dyad of the tetramer is 17%, whereas the corresponding content in the trimer is 37%. These results indicate, therefore, that the observed stereochemistry depends on the rate of *depletion* as well as the rate of *formation* of stereoisomeric anions.[15] This in turn would be consistent with a non-Bernoullian process in which the rate constant of formation of a meso or racemic dyad would depend on the stereochemistry of the last two or additional prior asymmetric carbon atoms of the oligomeric anion. This problem is currently under investigation.

Experimental Section

Synthesis. The oligomers were prepared as previously described.[3a] The lithio and potassio salts of 2-ethylpyridine were recrystallized by evaporation of a THF solution of the salts on the vacuum line followed by distillation onto the salt of enough hexane to dissolve the salt. After the apparatus was sealed, the solution was kept overnight in a freezer at −10 °C. Crystallization usually occurred, the crystals were washed with some cold hexane (obtained by distillation in the apparatus), and the washing solution was sealed off. The apparatus was then reevacuated on the vacuum line, and THF was distilled onto the crystals. The carbanion solution was then cooled to −78 °C and sealed. Carbanion concentrations were determined by determination of total base (at high concentration) or by UV–visible absorption at lower concentrations (10^{-2}–10^{-3} M).

The oligomerization reactions and the workup of the products were carried out as reported earlier.[3a] ^{13}Carbon-enriched methyl iodide (90%, Merck) was diluted with CH_3I to 25% ^{13}C content followed by drying over CaH_2 on the vacuum line. Protonation was carried out by distillation onto the solution of deareated water on the vacuum line.

Complete epimerization of the oligomers was carried out by in vacuo addition of *t*-BuOK dissolved in Me_2SO (0.1 M) onto the oligomers through breakseals. After 150–300 h, the reaction vessel was opened and water was added. The samples were extracted with diethyl ether. The ether solutions were washed several times with water to remove Me_2SO and were then dried with Na_2SO_4. After removal of ether on a rotatory evaporator, the residue was evacuated on the vacuum line, usually for 10 h or more.

Partial epimerization was carried out by using tubes with ground joints. Dried Me_2SO (1.5 mL) and *t*-BuOK (~0.2 g) were added under argon. The tubes were then capped with septum stoppers. Solvent aliquots (0.1 mL) were removed by syringe at various intervals and were injected into vials containing a two-phase ether–water system. The ether solutions were then directly used for GC analysis.

Chromatography. Preparative liquid chromatography was performed with an Altex Model 332 programmable gradient system fitted with a constant-wavelength (254 nm) UV detector, Model 153, with a 0.05-cm path length sample cell. For the separation of 1-g or subgram samples, a Lobar B column (Merck), 2.5 × 31 cm, containing 40–63-μm Lichroprep silica gel was satisfactory. Solvent gradient elution was carried out with hexane (A) and a 10:1 CH_2Cl_2–CH_3OH mixture (B) starting at 20% B and at flow rate of 5 cm^3/min. After about 30 min, the content of B was increased from 20 to 50% over a period of 60 min and held constant for an additional 30 min. Separation was excellent, and in some instances individual stereoisomers could easily be separated. The oligomer fractions after collection were condensed on a rotatory evaporator and were finally dried at 10^{-5}–10^{-6} mmHg on the vacuum line. Isotactic trimer and tetramer of better than 95% stereoisomeric purity were prepared by repeated preparative liquid chromatography using the methods described above.

Analytical liquid chromatography was carried out on a Waters liquid chromatograph Model ALC/GPC 201 (because of its "pulseless" flow) using a 25-cm column with 5-μm Ultrasphere packing (Altex). GC analysis was performed with a Hewlett-Packard Model 5710 A instrument equipped with a flame ionization detector, a Model 18740 B capillary column control, and a Model 33805 integrator. Columns were a 12-m dimethylsilicone-coated glass capillary column or a 25-m SE-54 silicone gum coated capillary column.

NMR measurements were carried out with a JEOL 100-MHz (25.2 MHz ^{13}C) spectrometer. ^{13}C NMR measurements (1000–8000 transients) were carried out with 4-s pulse delay. Longer pulse delays were found to be unnecessary. Gated decoupling experiments showed that nuclear Overhauser enhancement was found to affect the $^{13}CH_3$ absorptions of the various stereoisomers to the same extent. This is also demonstrated by the very good agreement with LC and GC determinations (Table I).

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References and Notes

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(8) We have adopted polymer stereochemical nomenclature in order to describe oligomers **5**–**10**. Thus, in the case of the protonated trimer **9**, the (m) isomer is thought of as generated from a meso dyad of a polymer by replacing the polymer chains flanking the dyad by a CH_3 and a CH_2–pyridine group. Although for symmetrical oligomers such as **6** the (mr) and (rm) stereoisomers are identical, they are not for a $^{13}CH_3$-terminated or protonated oligomer. Since the oligomers are written from left to right, the last symbol will refer to the dyad closest to the labeled or protonated end group.
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(15) Preliminary results on the stereochemistry of formation of higher oligomers and polymers indicate, however, that the lack of stereoregularity of monomer addition in the presence of Li ion is not caused by a preferential depletion of isotactic oligomeric anions.