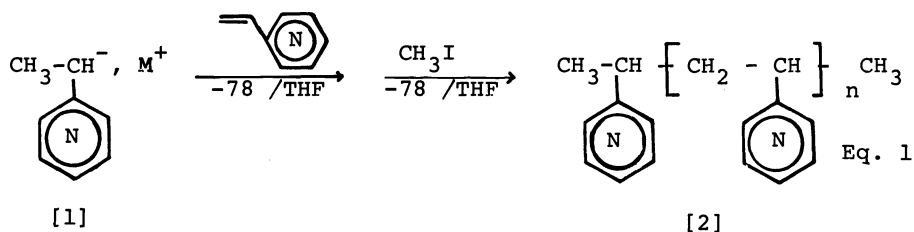


STEREOCHEMICAL EFFECTS OF ION PAIRING IN ANIONIC VINYL OLIGOMERIZATION AND RELATED CARBANION REACTIONS

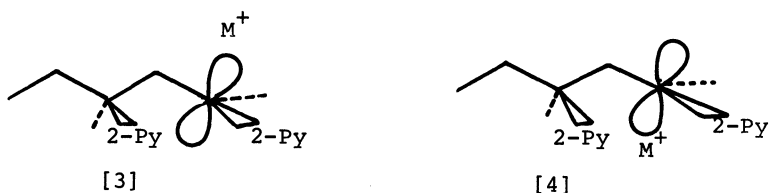
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Abstract - The oligomerization stereochemistry of the products of equation 1 was studied by ^1H and ^{13}C NMR. The stereochemistry of methylation and 2-vinylpyridine addition was found to be identical. With Li and Na as counterion both reactions lead to the formation of meso dyads so that the products are predominantly isotactic.

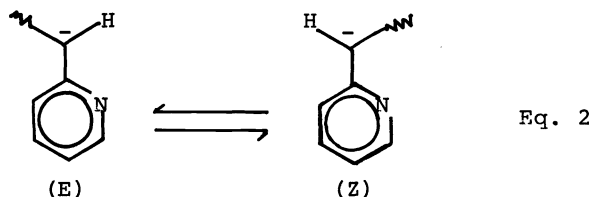


The alpha carbon stereochemistry is consistent with a cation side attack of electrophile on carbanion and on the basis of unequal proportions of diastereomeric ion pairs [3] and [4] in

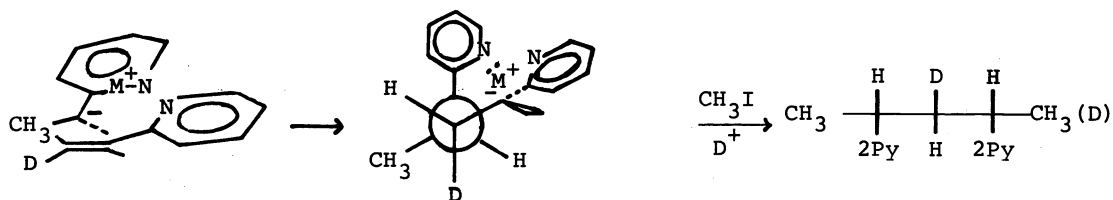


which the Li or Na counterion is coordinated with the penultimate 2-pyridine group leading to specific conformations in which [3] is preferred because of steric reasons. With larger or more extensively solvated counterions the interaction of metal ion with penultimate 2-pyridine group is decreased and [3] and [4] become more nearly equal in energy leading to a decrease in stereoselectivity.

Beta carbon stereoselectivity of products [2] prepared with beta deuterated vinylpyridines was also investigated. It was shown that this stereoselectivity may be related not only to the mode of presentation of monomer but also to anion geometry.



Equilibrium 2 demonstrated by ^1H and ^{13}C NMR was shown to be highly cation and solvent dependent the (E)/(Z) ratio decreasing with increasing cation size and cation coordination. It was shown that for the Li and K systems the beta carbon selectivity of the trans addition correlates well with equilibrium 2. Providing that metal ion - 2-vinylpyridine coordination occurs prior to addition this correlation is explained by equation 3.



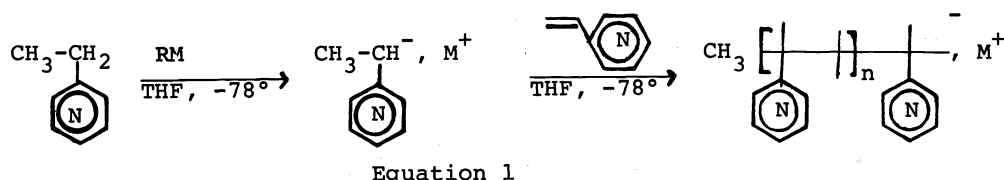
Equation 3

Since alpha carbon stereochemistry of the carbanion and beta carbon stereochemistry of the incoming monomer are simultaneously determined the lower (E)/(Z) ratio found for the K system is expected and found to lead to less selective placement of deuterium.

INTRODUCTION

The stereoselective anionic polymerization of methylmethacrylate in hydrocarbon media was described more than twenty years ago (1, 2, 3) and has since been demonstrated for several other vinyl monomers such as acrylates (4), vinyl t-butyl ketones (5), vinylpyridines (6, 7, 8), and so on. It soon became clear that the size of the alkali metal counterion and its state of coordination with solvent or complexing agent were important factors in determining the stereoregularity of the polymers. For instance the polymerization of MMA initiated by BuLi in toluene at -78°C gave isotactic polymers, but the corresponding polymerization initiated by Na or K compounds or by lithium salts in the presence of small quantities of cation coordinating solvents yielded polymers of substantially reduced stereoregularity (9).

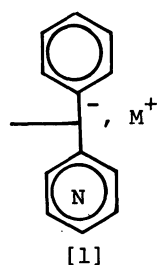
Rationalizations of the stereoselectivity of the BuLi initiated MMA polymerization in hydrocarbon media have been advanced by Cram and Kopecky (10), Goode *et al.* (11), Bawn and Ledwith (12), Furukawa (13), and Fowells *et al.* (4b). Although differing in detail, metal ion coordination by penultimate ester group is a common feature in these descriptions. However, the proposed stereoregulative mechanism is tentative since very little information is available concerning the structure of the carbanion site itself. Moreover, in these polymeric anions the extent of interaction with cation of coordinating penultimate, antepenultimate and prior groups of the copolymer is a complicating factor in the analysis of the polymerization stereochemistry. In previous work we have attempted to clarify this problem by investigating the oligomerization stereochemistry of vinylpyridines (14, 15, 16). Contrary to the acrylates and methacrylates the carbanions involved in the anionic polymerization of 2- and 4-vinylpyridines are quite stable and their carb-anion-pair structure may be conveniently investigated with spectrometric (17, 18) and conductometric (19, 20) techniques. Moreover the relative stability of these picolyl carbanions has enabled us to prepare and study the alkylation and vinyl addition stereochemistry of the butane-, hexane-, and higher oligomeric model anions (Eq. 1). This approach, at least in principle, permits a separation of the stereochemical effects of penultimate, antepenultimate, and prior groups of the chain. Equally importantly it permits a comparison between the stereochemistry of vinyl addition and that of other reactions of interest such as protonation and alkylation. In the following we wish to report the results of such studies and the correlation with spectrophotometric, conductometric, and ^{13}C and ^1H NMR studies of the carbanion-cation pair.



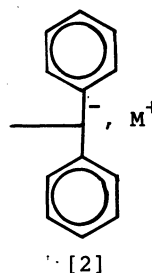
RESULTS AND DISCUSSION

Ion pair structure

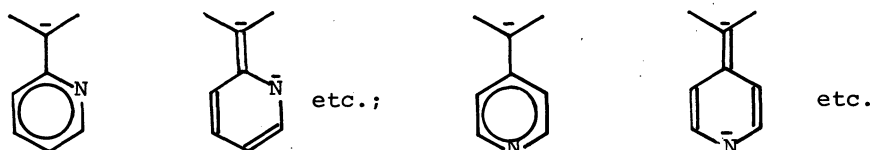
Previous investigations on carbanions [1] have shown that both 2- and 4-pyridyl substituted anions form tight ion pairs in ethereal solvents such as tetrahydrofuran, THF, dimethoxyethanes, and glymes (18). Only on addition of dibenzo-18-crown-6 to the Na or K salts of [1a] could separated ion pairs be observed whereas [1b] gave only externally complexed ion pairs. However, the Na salts of [1a] and [1b] formed separated ion pairs on addition of the [2.2.2]cryptand (21). In contrast the 3-pyridyl carbanion [1c] of Li and Na salts existed as separated ion pairs in THF, DME, and glymes and resembled ion pairing properties of hydrocarbon analog [2]. This pattern of ion pairing



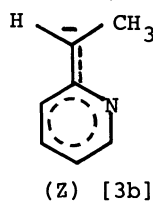
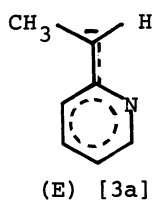
a = 2-pyridyl
b = 4-pyridyl
c = 3-pyridyl



suggests extensive delocalization of negative charge onto nitrogen for [1a] and [1b] in accordance with resonance structures below. This explanation is



supported by NMR studies on alkali salts of the 2- and 4-picolylyl carbanions in liquid ammonia by Zoltewicz and Helmick (22) and by Konishi et al. (23) on Li salts in THF that indicate considerable double bond character for the methine-ring carbon bond. The alkali salts of 2-ethylpyridine in THF were recently studied by ^1H and ^{13}C NMR (24). The spectra of Li and K salts are shown in Figures 1 and 2. The chemical shifts of the ring protons are in accordance with those reported by Konishi et al. (23). However, the difference between the two salts is of interest. For the Li salt only a single signal is observable for each of the ring protons but for the K salt a second less intense absorption signal is clearly observed especially for the 4- but also for the 3-proton up- and downfield, respectively. Analysis of the coupling pattern of the corresponding K salts in liquid NH_3 has indicated that the up- and downfield absorptions of the 4-proton are due to (Z) and (E) geometric isomers, respectively so that the (E)/(Z) ratio may be determined



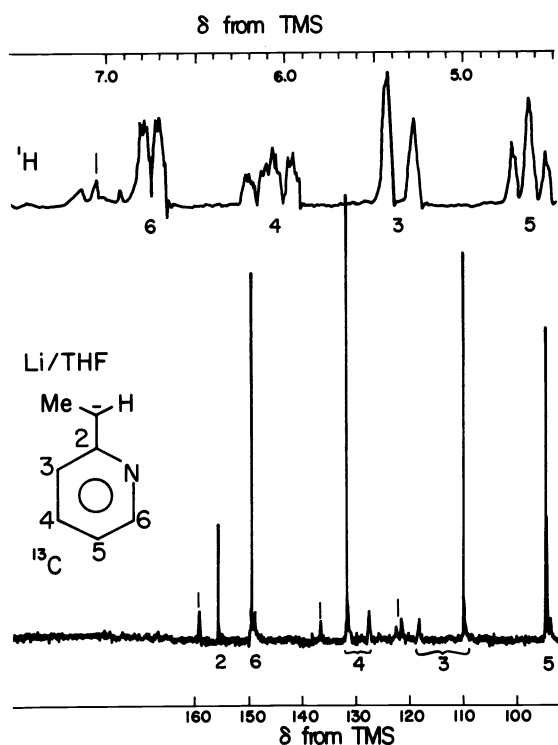


Figure 1: ^{13}C and ^1H NMR Spectra of Lithium 2-Ethylpyridine in THF- d_8

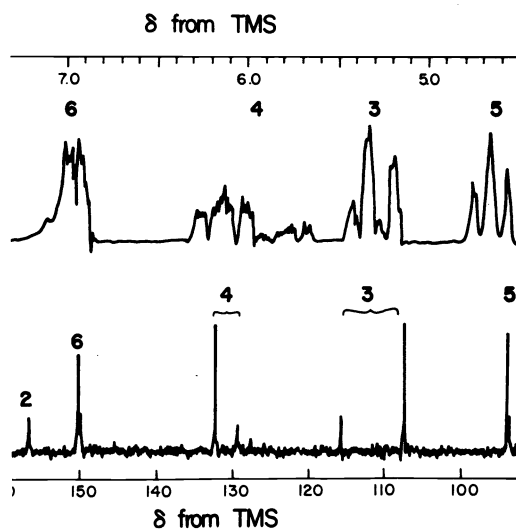


Figure 2: ^{13}C and ^1H NMR Spectra of Potassium 2-Ethylpyridine in THF- d_8

by integration of the 4- or 3-ring proton. Similar observations may be made from the ^{13}C NMR spectra. In this case the (Z) isomer of the Li salt in THF may be observed slightly upfield from the major signal.

Table 1 shows the NMR results for Li, Na, and K salts of 2-ethylpyridine and their complexes with glymes or macrocyclic coordinating molecules in THF.

TABLE 1. Effect of cation size and coordination on the (E)/(Z) ratio for 2-Ethylpyridine carbanion salts at 40°

Cation	Solvent	Coordinating Agent (Molarity)	(E)/(Z)
Li	THF		16
Na	THF		6
K	THF		4
Li	THF	Tetraglyme (2M)	4
Li	THF	(2.2.1)Cryptand (1 eq)	0.6
Na	THF	Tetraglyme (2M)	2
K	Liq NH_3		0.8

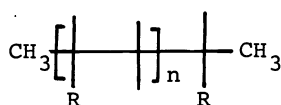
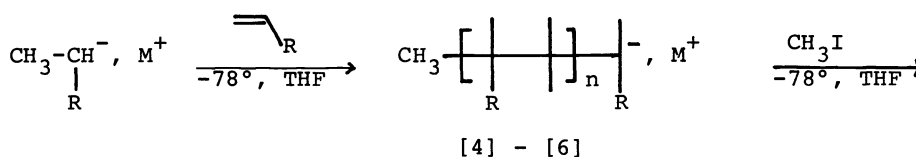
The (E)/(Z) ratio strongly depends on ion pair structure decreasing with increasing cation size and coordination. Similar trends have been observed by R. Ireland and coworkers for enolate salts (25) and by Schlosser and Hartmann for alkenyl salts (26). Although the detailed reason for this behavior is not clear the results appear to indicate a cation location toward the nitrogen atom thereby minimizing non bonded interactions of metal ion coordination sphere and the CH_3 group. More extensive coordination of the cation leads to a greater interionic distance and now the steric interaction with the CH_3 group may be minimized so that the (E)/(Z) ratio is reduced. Such a separated or loose ion pair may resemble a free anion. In agreement with this

prediction, CNDO calculations on this anion indicate approximately equal stability for (E) and (Z) isomers (27), the (Z) form being preferred by 0.14 Kcal. The (E)/(Z) ratio was found to be remarkably temperature independent. No major changes in their rates were observed for the K salt from -60° to $+80^\circ$. The substantial degree of double bond character is indicated by the high coalescence temperature of the 4- or 3-proton ($90^\circ - 110^\circ$ depending on cation and solvent).

STEREOSELECTIVE OLIGOMERIZATION

Alpha carbon

Model anions [4] - [6] were prepared by slow *in vacuo* distillation of a calculated amount of monomer onto the 2- or 4-ethyl pyridyl alkali salt in THF at -78°C and were reacted with CH_3I , again by distillation of the alkyl halide onto the carbanion at -78° , until the red color of the carbanion had disappeared. After workup of the reaction product the pentanes ("dimers") [7] were obtained by distillation and the heptanes (trimers) [8], nonanes (tetramers) [9], and higher oligomers were obtained by column chromatography (Experimental Results). The structure and stereochemistry of the oligomers were determined by 60, 100, and 270 MHz ^1H NMR and by 25.2 ^{13}C NMR.



R = 2-pyridyl

Eq. 2

[4] n = 1

[5] n = 2

[6] n = 9-11

[7] n = 1, [8] n = 2

[9] n = 3, [10] n = 5-6

[11] n = 9-11

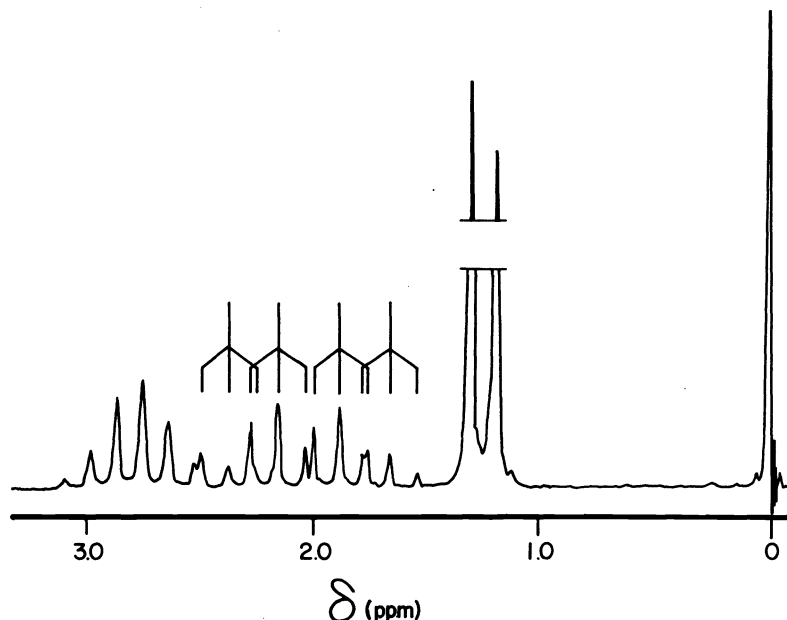


Figure 3: ^1H 60 MHz NMR spectrum of meso 2,4-di-(2-pyridyl) pentane in CCl_4 .

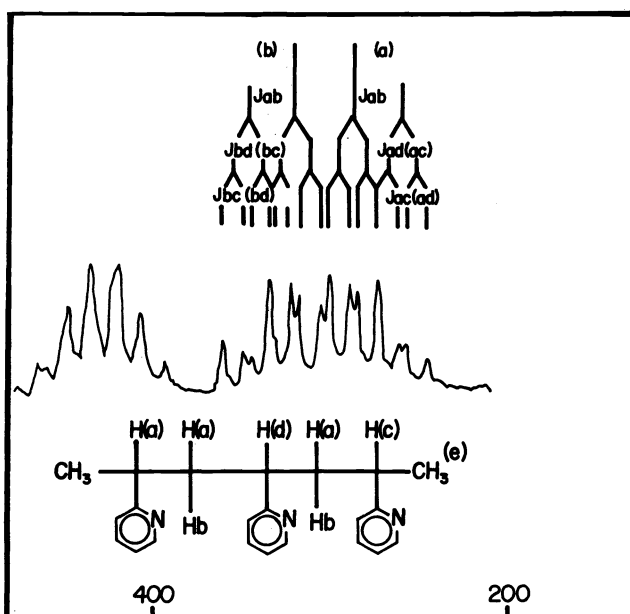


Figure 4: ^1H 100 MHz nmr spectrum of the CH_2 portion of isotactic 2,4,6-tri-(2-pyridyl)heptane in CCl_4 .

Table 2: Methylation stereochemistry of the 1,3-di-(2-pyridyl)-butane anion [4] as a function of cation and cation coordination.

Cation	Anion	Solvent	Coordinating Agent	T °C	% Meso
Li	[4]	THF		-78°	>99%
Li	[4]	THF		0	95%
Na	[4]	THF		-78°	96%
K	[4]	THF		-78°	65%
Rb	[4]	THF		-78°	57%
Na	[4]	THF	18-crown-6 (1 eq)	-78°	58%
Li	[4]	THF	Pyridine (50% vol)	-78°	83%
Li	[13] ^a	THF		-78°	~50%

^a1-(4-pyridyl)-3-(2-pyridyl)butane anion [13]

The results are shown in Figures 3 - 6 and in Tables 2 and 3. The stereochemistry of the meso-2,4-di-(2-pyridyl)pentane prepared with Li and Na as counterions is clear from the methylene portion of the 60 MHz spectrum and from the well resolved methyl doublet (Fig. 3). For the larger and more extensively coordinated cations the methylene portion of the pentane product is more complex due to the presence of the racemic stereoisomer. However, the two methyl doublets centered at $\delta = 1.25$ and 1.19 corresponding to meso and racemic dimer, respectively, are clearly distinguished so that the proportion of stereoisomer could conveniently be determined by integration. Table 2 indicates that the methylation stereochemistry of [3a] is highly dependent on cation size and coordination but not on the temperature of the vinyl pyridine addition and time and temperature of storage of anion [3a]. Therefore the observed stereoselection is due to the methylation reaction. Equilibrium epimerization of meso-[7] with potassium tert-butoxide in DMSO resulted in equal proportions of meso and racemic stereoisomer so that the two stereoisomers appear to be of about equal stability. A similar result was obtained by Flory and coworkers for the epimerization of the

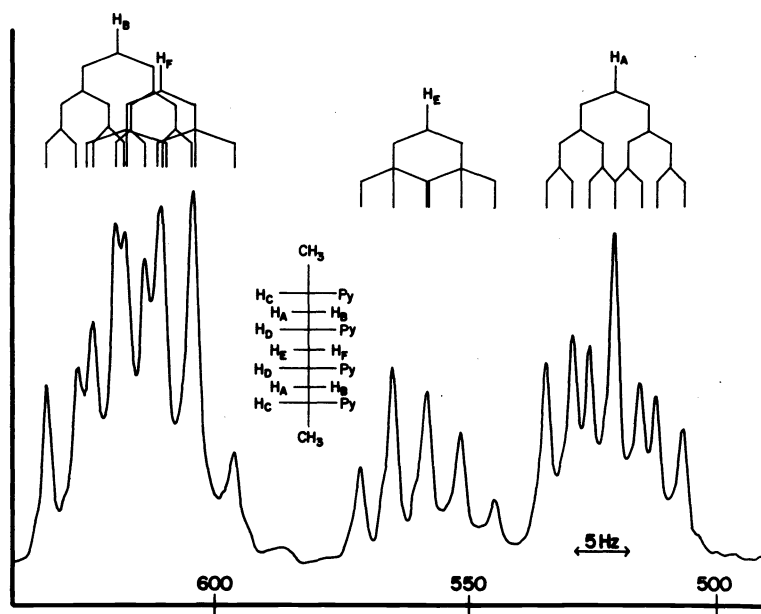


Figure 5: ^1H 270 MHz NMR spectrum of the CH_2 portion of isotactic 2,4,6,8-tetra-(2-pyridyl) nonane in CCl_4 .

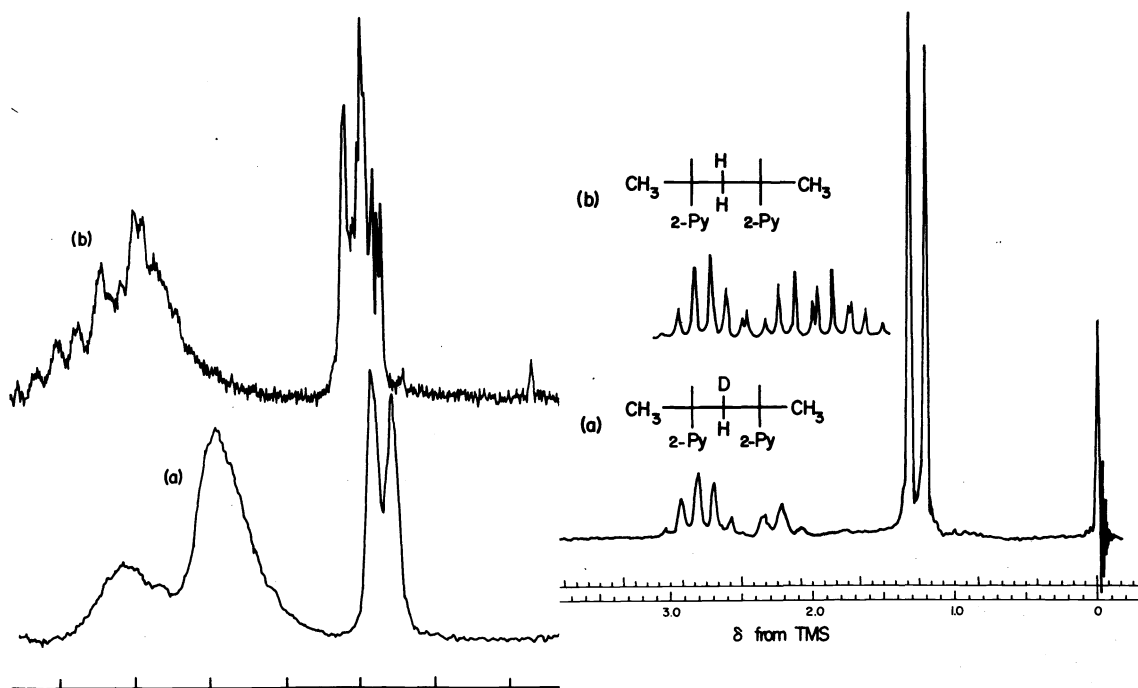


Figure 6: 60 MHz ^1H NMR spectra of penta-hexamer (a) and epimerized tetramer (b) in CCl_4 .

Figure 7: (a) ^1H 60 MHz NMR spectrum of meso-3-d $_1$ -2,4-di-(2-pyridyl) pentane in CCl_4 ; (b) ^1H 60 MHz NMR spectrum of meso-2,4-di-(2-pyridyl) pentane in CCl_4 .

corresponding 2,4-diphenylpentane (28). The methylation reaction therefore appears to be "kinetically" controlled. Table 2 shows the importance of the position of the nitrogen atom in the ultimate and penultimate pyridine ring. Thus methylation of the 1,3-di-(4-pyridyl) butane anion [12] and 1-(4-pyridyl)-3-(2-pyridyl)butane anion [13] lithium salts leads in each case to equal proportions of diastereomeric products.

Table 3: Methylation stereochemistry of hexane anion [5] as a function of cation and cation coordination.

Cation	Solvent	I (mm)	H (mr, rm)	S (rr)
Li	THF	>95	<5	<5
Na	THF	>95	<5	<5
Na	THF	~50	~50	--
Na, 18-C-6 ^a				
t-BuOK ^b	DMSO	~25	~50	~25

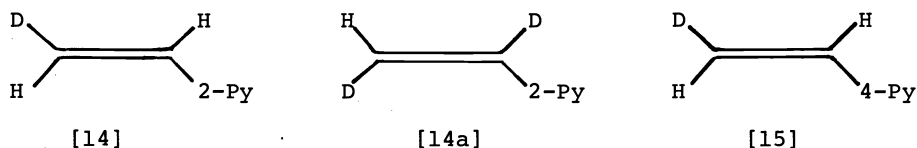
^aOne equivalent of 18-crown-6 present during methylation only.

^bEpimerization of isotactic trimer for about 2 weeks in t-BuOK/DMSO at 25°C.

The effects of cation and cation coordination on the methylation stereochemistry of hexane anion [5] is shown in Table 3. Figure 4 shows the 100 MHz ¹H NMR spectrum of isotactic trimer [8] prepared with Li as counterion in THF. Apparently the reaction of the Li and Na salts of butane anion [4] with both CH₃I and 2-vinylpyridine leads to a meso sequence and the methylation stereochemistry of the Li and Na salts of [4] and [5] appears to be identical. This is also apparent from the product prepared by vinyl addition in the presence of Na counterion without and methylation in the presence of 18-crown-6. The first addition is stereoselective and from inspection of Table 2 the methylation should result in the formation of equal proportions of meso and racemic dyads. The expected mixture of isotactic and heterotactic trimer was indeed found to be equimolar. Again epimerization of the isotactic trimer results in the formation of the mm, mr, and rr stereoisomers in the expected statistical distribution of 1:2:1 (Table 3) so that here also kinetic control is indicated for the stereoselective addition. The ¹H 270 MHz spectrum of the methylation product of the Li salt of [6] is shown in Figure 5 and the spectrum of the pentamer-hexamer mixture is shown in Figure 6. The tetramer is clearly predominantly isotactic from inspection of the methylene portion of the spectrum. The higher oligomers appear to be largely isotactic from the well resolved CH₃ doublets and the chemical shift of the methylene portion of the spectrum that differs appreciably from that of the t-BuOK/DMSO epimerized tetramer (Fig. 5). The ¹H and ¹³C NMR spectra of a higher molecular weight product [11] (average degree of polymerization about 10) prepared under identical conditions likewise appears to be predominantly isotactic.

Beta-carbon stereochemistry

The dimer, trimer and tetramer of E-β-d₁-2-vinylpyridine [14] (~90%) were prepared as described above. The dimer spectrum was studied with 60 MHz NMR spectrometry (Figure 7) and the trimer and tetramer were investigated with 270 MHz NMR. The assignment of erythro (e) and threo (t) for the downfield



and upfield methylene absorption, respectively, was based on the analogous meso 2,4-dicarbomethoxypentane for which an absolute assignment was made (36). Integration of the tetramer spectrum leads to the surprising conclusion that for the inner methylene protons the assignment of downfield and upfield

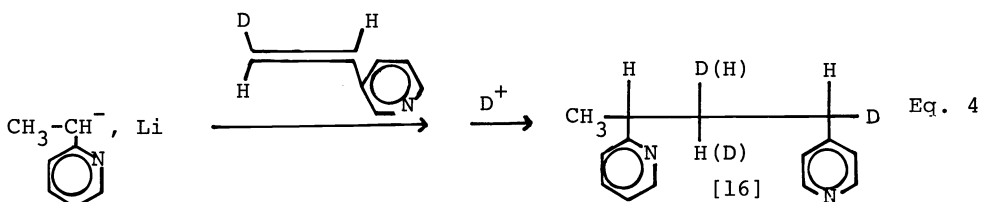
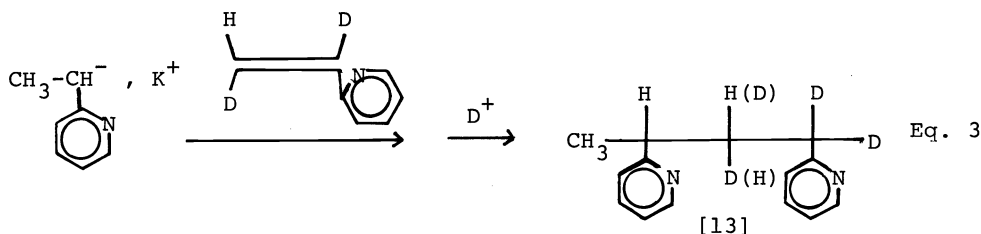
absorption for (e) and (t) proton is reversed. While the reason for this reversal is not clear this assignment is identical with the one proposed by Matsuzaki and Sugimoto (29) for isotactic poly(2-vinylpyridine). The

Table 4: Beta-carbon stereochemistry for the anionic oligomerization of beta-deuterated vinylpyridines in THF at -78°C

Anion ^a	Cation	Monomer	Predominant Formal Addition Stereochemistry	Selectivity
Monomer ⁻	Li	[14]	trans	91%
[4]	Li	[14]	trans	67%
[5]	Li	[14]	trans	90%
Monomer ⁻	K	[14a]	trans	75%
Monomer ⁻	Li	[15]	trans	51%

^aMonomer⁻ refers to 2-ethylpyridine carbanion; [4] and [5] are butane and hexane anion, respectively.

results are shown in Table 4 along with the formal stereochemical overall addition of the deuterated monomer which is predominantly trans. The first addition is highly β -carbon stereoselective ($\sim 91\%$). The selectivity for the second and third additions are 67 and 90%, respectively. Apparently, the second step is substantially less stereoselective than the first. While the apparent increase in stereoselectivity for the third addition is intriguing it should be noted that the error in calculating the selectivity increases with the number of additions since corrections are made for all previous steps in the formation of the oligomer. The effect of cation on β -carbon stereoselectivity was determined through preparation of the 1,3-di-(2-pyridyl)butane [13] through addition of Z- α,β -d₂-2-vinylpyridine [14a] (eq. 3). In this way the difficulty of obtaining a mixture of racemic and meso pentanes is avoided. Investigation of this sample by 270 MHz spectroscopy again established trans addition as being preferred but the stereoselection is substantially less than that for Li ($\sim 77\%$). Apparently, as was also observed for the alpha carbon stereochemistry, stereoselection is less for larger cations possibly due to weaker interaction of vinyl monomer with cation prior to addition. In order to investigate the importance of monomer structure, E- β -d₁-4-vinylpyridine [15] ($\sim 65\%$) was added to the Li salts of 2-ethylpyridine at -78°C THF and deuterated to form [16] (Eq. 4). Table 4 shows that this addition reaction is non selective indicating that the position of nitrogen with respect to the vinyl group is important in the β -carbon stereochemistry.

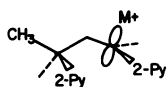


DISCUSSION

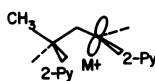
Alpha carbon stereochemistry

The highly stereoselective methylation and vinyl addition reactions are unusual in these type media. Moreover the stereochemistry of these two reactions is remarkably similar. We propose the following rationalization for these observations. Unpaired carbanions of the type investigated here are most likely sp^2 hybridized planar and, therefore achiral species. However, the ion pairs are, in principle, chiral provided that the cation is located above (or below) the anion as seems likely (30, 31). The presence of a single penultimate center then leads to ion pairs [17] and [18] which are diastereomeric and thus, at least in principle, of unequal energy. The relative stability of the ion pairs is difficult to predict without some knowledge as to their conformation. Previous conductometric studies by Fisher and Szwarc (10) and Sigwalt and coworkers (20) have shown that the Na counterion is coordinated to the penultimate 2-pyridyl group. The corresponding models are schematically shown below. The structure [17a] is expected to be more stable due to butane gauche and CH_3 -1-(2-pyridyl) interactions in [18a].

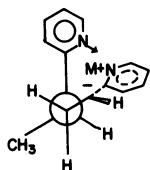
From inspection of space filling (CPK) models it appears that [18b] which is configurationally identical with [18a] is expected to be less stable than



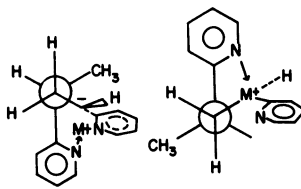
[17]



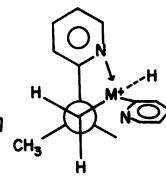
[18]



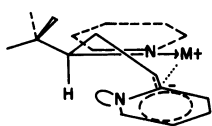
[17a]



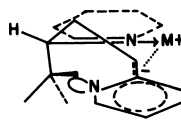
[18a]



[18b]



[17a]



[18a]

[17a] due to the larger distance between metal ion and penultimate 2-pyridyl group. Other models with the cation in the nodal plane and pyramidal carbanion are ruled out since they are inconsistent with NMR data on the carbanion salt and/or inconsistent with the observed stereochemistry (see below). The stereochemistry of these reactions is, in addition, determined by the direction of electrophilic attack with respect to cation. A cation side (syn) attack would appear more likely since anti attack would lead to a product separated metal iodide ion pair which is expected to be much less stable than a tight ion pair (32). A similar rationale has been offered to account for the kinetics (33) and stereochemistry (34) of protonation of carbanions by alcohols. The reaction is thus most likely due to a cation side attack of CH_3I or 2-vinylpyridine on the more stable ion pair diastereomer [17a]. The resulting meso sequence is in accord with our experimental findings. For instance: (1) The presence of antepenultimate or prior 2-pyridine group does not appear to influence the reaction stereochemistry of methylation or 2-vinylpyridine addition. This is consistent with the proposed model although for higher molecular weight anions interactions of the cation with these 2-pyridine groups on the polymer are not excluded. (2) With the 4-pyridyl group as a carbanion substituent or in both ultimate and penultimate positions the methylation reactions are not stereoselective. The cation coordination by penultimate 4-pyridine group is highly unlikely from inspection of models. The lack of stereoselective methylation of 1-(4-pyridyl)-3-

(2-pyridyl)butane anion is curious but may be due to a different cation position or to a tighter ion pair found for the 4-pyridyl carbanions (18). (3) The cation size and cation solvation dependence of the methylation stereochemistry may be explained by the effects of these parameters on cation complexation by penultimate 2-pyridyl group. For large cations such as K or Rb or for extensively coordinated cations such coordination is undoubtedly reduced or absent.

For higher molecular weight polymers prepared under identical conditions the NMR spectra are quite broad and differ considerably from isotactic poly-(2-vinylpyridine) polymers initiated by organomagnesium reagents in hydrocarbon media (29). This surprising apparent difference between oligomers and polymers may be due to a change in stereoselection at a certain degree of polymerization or to side reactions. Preliminary results on isotactic poly-(2-vinylpyridine) in the presence of 2-ethylpyridyl lithium in THF indicate that substantial crosslinking occurs even at -78° for 1 hour. Moreover, during the preparation of the 2-vinylpyridine oligomers we have invariably found substantial proportions of side products that appear to be complex mixtures. Thus it appears that the possibility of side reactions during polymerization needs to be seriously examined.

Beta carbon stereochemistry

Previous work by Schuerch and Bovey and their coworkers (4b, 35) and Yoshino et al. (4a) have shown that for the anionic polymerization of beta deuterated acrylates and methacrylates beta-carbon stereochemistry is related to the mode of presentation of the monomer to the chain end carbanion. A comparison of the products formed by addition of (E)- β -d₁-2-vinylpyridine or (E)- β -d₁-4-vinylpyridine to the 2-ethylpyridyl-lithio salt provides evidence for this proposition. While the addition of the first monomer leads to significant beta carbon stereoselection ($\sim 90\%$) (E)- β -d₁-4-vinylpyridine does not. Further consideration of the reaction however, suggests that monomer presentation mode may not be the only factor. The (E)-(Z) equilibrium should play an important role as well. Figure 8 shows the addition of the (E)-d₁-2-vinylpyridine to an 2-ethylpyridyl salt in the (E) form. Provided that the cation is

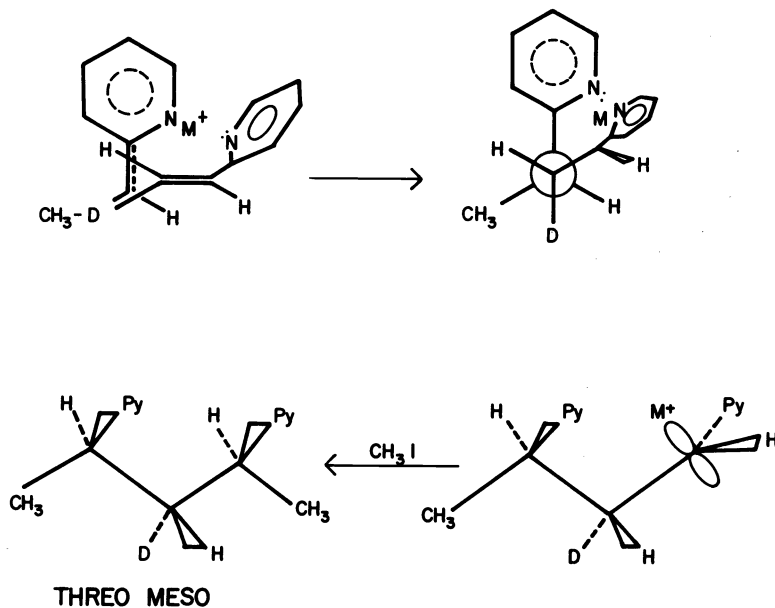


Figure 8: Proposed mechanism for the beta-carbon stereoselective addition of (E)- β -d₁-2-vinylpyridine to the 2-ethylpyridine carbanion.

positioned off the line bisecting the CH₃-C-H angle and near the nitrogen atom of the anion, and that monomer coordination to cation occurs during the addition, as seems reasonable, the deuterium atom is placed in the threo position of the pentane product (7). Since the stereochemistry of the alpha carbon of the salt and the beta carbon of the monomer are simultaneously determined a predominance of the (Z) form in the salt should lead to the opposite stereochemistry of the beta carbon position all other things being equal. Attack of the monomer on the (E) carbanion below the plane should result in the same threo-meso product since in that case both the stereochemistry of alpha and beta carbon are inverted. The results appear to support the proposed mechanism. First if the cation were symmetrically positioned above the ring monomer approach from the left side (Fig. 8) would be feasible leading to opposite (erythro) placement of deuterium in the product and the reaction would not be expected to be beta carbon stereoselective. Second the proposed scheme is supported by a close correlation between the (E) - (Z) equilibrium and beta carbon stereochemistry for the addition of (E)- β -d₁-2-vinylpyridine to the Li and K ethylpyridyl salts. The percentages of (E) carbanion and threo-meso product for the Li and K salt are 94% - 91% and 80% - 77%, respectively (Tables 1 and 4).

The effect of degree of oligomerization on beta carbon stereochemistry is less clear. The second step appears to be less stereoselective (~67%) but the selectivity of the third step is again 90%. Although it is possible that complexation of 2-vinylpyridine to the counterion is more difficult because of competition by penultimate 2-pyridyl group this interpretation has to await data on the (E) - (Z) equilibria in the butane and hexane anions. Unfortunately, a study of these anions is complicated due to carbanion stability problems. Further work on these problems and the related oligomerization of analogous acrylate and methacrylate monomers is in progress.

EXPERIMENTAL

Solvents

THF was distilled into the reaction vessel in vacuo from a solution of the Na-K salt of benzophenone dianion. Toluene, pyridine, and glymes were stirred over CaH₂ overnight, degassed, and distilled in vacuo.

2-Ethylpyridine

2-Ethylpyridine was fractionally distilled, stirred over CaH₂, degassed, and distilled in vacuo. Before use, it was treated with a carbanion salt such as alpha methyl styrene tetramer sodium and distilled into ampoules equipped with breakseals.

2-Ethylpyridine salt

The lithium salt was prepared from n-BuLi in THF at -78°. The sodium, potassium, and rubidium salts were prepared from the respective alpha methylstyrene tetramer salts and 2-ethylpyridine. The salts used for NMR studies were purified by recrystallization in vacuo, from toluene and/or hexane.

Deuterated vinylpyridines

E- β -d₁-2-vinylpyridine (91%) was prepared by Cr^{II} reduction of d₁-2-ethynylpyridine (37) that was prepared in turn by exchange of 2-ethynylpyridine in D₂O in the presence of triethylamine. 2-Ethynylpyridine was synthesized by the method of Leaver *et al.* (38). Z- α,β -d₂-2-vinylpyridine (65%) was similarly prepared by the trans reduction of 2-ethynylpyridine in D₂O. E- β -d₁-4-vinylpyridine (65%) was prepared by the Cr^{II} reduction of d₁-4-ethynylpyridine.

Oligomers

Oligomers were prepared by a slow (~1-2 hours) in vacuo distillation of 1-3 g of monomer onto the carbanion solution kept at -78°C and terminated by distillation of CH₃I through the vacuum line. The solvent was removed under reduced pressure and the product was dissolved in HCl. The solution was washed with ether neutralized with Na₂CO₃ and extracted into ether. After drying over MgSO₄ and removal of ether, the dimer [7] was obtained by vacuum distillation (110-114°C/0.25 mm Hg). Trimer, tetramer, and higher oligomers were isolated by liquid column chromatography. Neutral alumina of Brockman Activity I (80-200 mesh) which had been stored in a 110°C oven overnight was used. The elution began with a 50/50 (vol/vol) mixture of ether and ligroin. The composition was varied until 100% ether. A 50/50 mixture of ether and ethylacetate was then used.

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