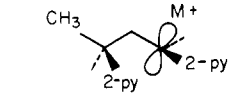
for possible coupling of two carbonyls. Fragmentations on bi- and trinuclear metal aggregates need to be studied.[11,12]

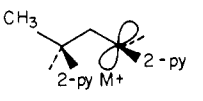
Acknowledgment. This work was supported by the National Science Foundation (Grant CHE 7828048).

(11) Acetylene fragmentations, coupled with cluster formation, are known: King, R. B.; Harmon, C. A. *Inorg. Chem.* **1976**, *15*, 879-885. Fritch, J. R.; Vollhardt, K. P. C.; Thompson, M. R.; Day, V. W. *J. Am. Chem. Soc.* **1979**, *101*, 2768-2770. Yamazaki, M.; Wakatsuki, Y.; Aoki, K. *Chem. Lett.* **1979**, 1041-1044. See also the unique coupling of two carbynes to a binuclear acetylene complex: Fischer, E. O.; Ruhs, A.; Friedrich, P.; Huttner, G. *Angew. Chem.* **1977**, *89*, 481-482.

(12) For a theoretical discussion of acetylene fragmentation on certain metal surfaces, see: Anderson, A. B. *J. Am. Chem. Soc.* **1977**, *99*, 696-707. *J. Catal.* **1981**, *67*, 129-144.



4X



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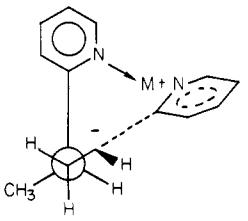

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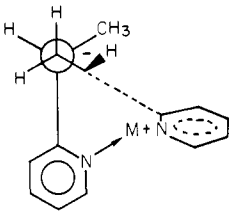

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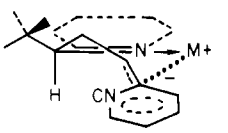

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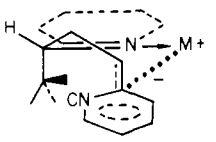

4Y

Oligomerization of Vinyl Monomers. 2. Evidence for a Conformationally Restrained Six-Membered Ring Containing Lithium Ion

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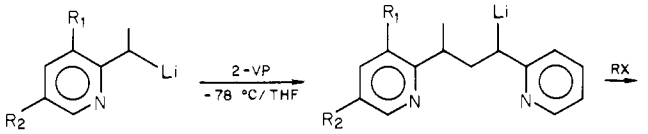
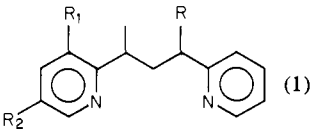
There has been much recent interest in stereoselective alkylations of lithiocarbanion salts and similar electrophilic reactions.[2,3] Several of these have been formulated in terms of an intramolecular coordination of the metal ion by a chelating group, thus



1-3 4-6



(1)

7-9

(a) R = CH_3; (b) R = CD_3
1, 4, 7, $R_1 = R_2 = H$
2, 5, 8, $R_1 = CH_3$; $R_2 = H$
3, 6, 9, $R_1 = H$; $R_2 = CH_3$

providing an asymmetric environment at the reacting carbanion.[2,4,5]

We now wish to report evidence for such a scheme involving the addition of 2-vinylpyridine (2-VP) to anions **1-3** at -78 °C in THF and sequential methylation according to reaction 1. Previous work[4a,6] had indicated a very highly stereoselective (>99%) methylation of **4**, yielding meso **7**. The corresponding methylation in the presence of larger or cryptated and crowned cations had been shown to occur in a largely nonstereoselective manner. The remarkable selectivity of the methylation reaction in the presence of Li or Na ion was ascribed as due to the formation of a conformationally restrained cyclohexene-like ring containing Li ion **4X**, which should be preferred over its diastereomer **4Y**, generated by exchange of CH_3 and methine H, in which butane guache and CH_3-nitrogen lone pair interactions are expected to decrease its stability. Substitution of the 3′ proton of the chelating pyridine ring by a group of modest size, such as methyl, in **4X** is expected to substantially decrease the stability of the chelated complex relative to that of the unsubstituted analogue due to nonbonded interactions with the methylene and the methyl group. Substitution of the 5′ proton, however, should have no effect. A similar substitution of the 3′ position in **4Y** is not expected to lead to severe nonbonded interactions. Accordingly, anions **2** and **3** prepared by reaction of the carbon acid in THF at -78 °C with *n*-BuLi were reacted with 1 equiv of 2-VP by slow in vacuo distillation followed by reaction with CH_3I. The products were isolated, separated by preparative medium-pressure liquid chromatography, and analyzed by ^1H and ^{13}C NMR spectroscopy and by GC utilizing a 25-m capillary column. The results are shown in Table I.

The 100-MHz ^1H NMR spectrum of **7** in $CDCl_3$ showed a methyl doublet (δ 1.30) and a methylene multiplet (δ 2.11) characteristic for meso **7**.[6] The corresponding spectrum of **8b** showed two methyl doublets at 1.16 and 1.26 ppm in the ratio of 3:1, and the gas chromatogram of the mixture likewise showed a 3:1 ratio of isomers.[7,8] Corresponding observations were made

(1) Present address: CRM, 6 Rue Boussingault, Strasbourg, France.

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(4) (a) Hogen-Esch, T. E.; Tien, C. F. *J. Am. Chem. Soc.* **1976**, *98*, 7109. (b) Hogen-Esch, T. E.; Jenkins, W. L. *Ibid.* **1981**, *103*, 3666.

(5) Lynch, T. J.; Newcombe, M.; Bergbreiter, D. E.; Hall, M. B. *J. Org. Chem.* **1980**, *45*, 5005.

(6) Hogen-Esch, T. E.; Tien, C. F. *Macromolecules* **1976**, *9*, 871; **1980**, *13*, 207.

(7) Stereoisomeric relationships were confirmed by mass spectrometry and base-catalyzed epimerization (Table I). The stereoisomers could also be distinguished by the proton chemical shifts of their picoline methyl groups at 1.95 and 2.10 ppm.

(8) The 3:1 ratio of stereoisomers was identical when the crude reaction mixture was directly injected into the GC column so that the ratio of stereoisomers was unaffected by the LC separation.

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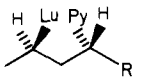
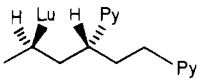
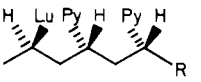
Table I. Stereochemistry of Products 7-9 and 13-18[a,b]



(a) 2(*R*),4(*R*)-8 (R = CH_3)
(b) 2(*R*),4(*R*)-8 (R = CD_3)
Lu = Lutidine
Py = pyridine



2R, 4R - 14



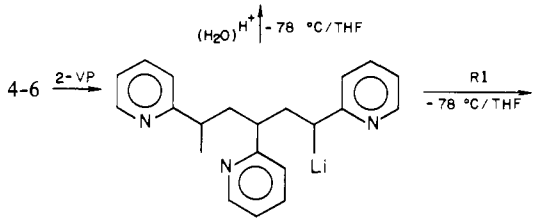
(a) 2(*R*),4(*R*),6(*R*)-17 (R = CH_3)
(b) 17 (R = CD_3)

	products					
stereoisomer[c]	7	8	9	13	14	15
2*R*, 4*R* (racemic like)	<0.01 (0.50)	0.76 (0.52)	0.01 (0.49)	0.36 (0.53)	0.73 (0.55)	0.30 (0.42)
2*R*, 4*S* (meso like)	>0.99 (0.50)	0.24 (0.48)	0.99 (0.51)	0.64 (0.46)	0.27 (0.45)	0.70 (0.57)

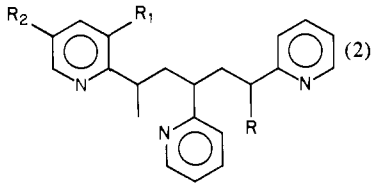
stereoisomer	16	17	18
2*R*, 4*R*, 6*S* (syndiotactic like)	~0.01 (0.28)	0.02 (0.29)	0.01 (0.27)
2*R*, 4*R*, 6*R* (heterotactic like)	0.42 (0.50)	0.71 (0.25)	0.39 (0.50)
2*R*, 4*S*, 6*R* (heterotactic like)		~0 (0.24)	
2*R*, 4*S*, 6*S* (isotactic like)	0.57 (0.22)	0.27 (0.22)	0.60 (0.23)

[a] Determined by capillary gas chromatography. Stereoisomers identified on the basis of NMR spectroscopy (see ref). [b] Fractions of epimerized products in brackets. Epimerization in the presence of K-*t*-BuO/Me_2SO at 25 °C for 300 h. [c] Carbons numbered from left to right. enantiomers are omitted. The terms syndio, hetero-, and isotactic-like refer to the corresponding symmetrical analogues 16. (See, for instance; Bovey, F. "Polymer Conformation and Configuration"; Academic Press: New York 1969).

13-15



10-12



16-18

(a) R = CH_3; (b) R = CD_3
10, 13, 16, $R_1 = R_2 = H$
11, 14, 17, $R_1 = CH_3$; $R_2 = H$
12, 15, 18, $R_1 = H$; $R_2 = CH_3$

by using ^{13}C NMR spectrometry. The stereochemical relationship of the two components in **8a** (**8b**) were confirmed by epimerization in Me_2SO/*t*-BuOK at 25 °C for ~300 h, which resulted in an approximately equimolar mixture of the two isomers (Table I). A corresponding investigation of **9** showed the presence of only one isomer (>99%). The striking similarity of the ^1H spectrum of this compound with that of meso-**7** indicated that the stereochemistry of formation of **7** and **9** are indentical. Although the two diastereomers of **8** cannot be identified with certainty, a comparison of its NMR and GC data with that of the known isomers of **7** and **9** strongly suggests that the racemic-like isomer (*R*,*R* or *S*,*S*) is the major one.[9] It is clear in any event that the introduction of a methyl group in the 3′ position of the complexing 2-pyridine ring leads to a dramatic decrease in methylation stereoselectivity consistent with the intermediacy of **4X**.

Investigation of the protonated trimer products **13–15** and the corresponding methylated trimers **16–18** (reaction 2) showed that addition of 2-VP to **4**, **5**, and **6** is not stereoselective (Table I). A similar result had previously been obtained for the corresponding addition of 2-VP to **4**.[10,11] However, the stereochemical composition of products **15** and **18** is found to be virtually identical with that of **13** and **16**, respectively, both from their ^1H and ^{13}C spectra and from the relative intensities and retention times of their gas chromatograms. The distributiuon of stereoisomers is quite different in compounds **14** and **17**, however, and is similar to that in **8** (Table I). The major and minor stereoisomers in **14** and **17** are assigned as 2*R*,4*R* and 2*R*,4*S*, and 2*R*,4*R*,6*R* and 2*R*,4*S*,6*S*, respectively,[12] on the basis of the NMR and GC data.[13] Thus, in contrast to the methylation of anion **5**, that of **11** is highly stereoselective and probably occurs with a stereochemistry identical with that of **10** and **12**. This shows in turn that as long as the prochiral carbanion is flanked by an asymmetric center bonded to a 2-pyridine ring unsubstituted in the 3′ position, the methylation is highly stereoselective consistent with the intermediacy of the chelated complex.

Acknowledgment. Support by the National Science Foundation sponsored U.S.-France Exchange Program (C.M.) and the National Science Foundation Polymers Program is gratefully acknowledged.

(9) For instance, the methyl groups of the predominant stereoisomer of **8**, like those of the racemic stereoisomers of **7** and **9**, absorb upfield. Moreover, the major stereoisomer of **8**, like the racemic stereoisomers of **7** and **9**, has the lower GC retention time and predominates slightly upon epimerization (Table I).

(10) Huang, S. S. Ph. D. Dissertation, University of Florida, 1981.
(11) Huang, S. S.; Mathis, C.; Hogen-Esch, T. E. *Macromolecules*, in press.
(12) Enantiomers are omitted.
(13) The stereochemical assignments are primarily based on the relative GC retention times in **13** and **14** and **16** and **17**. The NMR data were inconclusive. A comparison of the stereoisomers of **14** and **17**, however, clearly indicates a highly stereoselective methylation regardless of these assignments.