

Table V
Synthesis of Allyl Alcohols by Addition of α -Lithio
Selenoxides to Ketones and Aldehydes^{16e, 60b}

lithium reagent	carbonyl compound	allyl alcohol	yield, %
			78
			74
			68
			69
			76

Summary. The combination of readily accessible reagents and convenient reactions for the introduction of selenium, the air stability and ease of manipulation of most organoselenium compounds, and the availability of mild oxidative and reductive reactions for the removal of selenium has begun to make selenium one of the more valuable of the heavier elements to the synthetic organic chemist. It is expected that refinement and elaboration of the methods outlined here will continue and that additional new procedures based on the sometimes unique reactivity of organoselenium compounds will be developed.

It is a pleasure to thank my co-workers (J. M. Renga, I. L. Reich, S. K. Shah, F. Chow, J. E. Trend, P. D. Clark, S. Wollowitz, P. A. Gold, M. L. Cohen and S. L. Peake) for their conceptual and experimental contributions to this work, and to the National Science Foundation, The Petroleum Research Fund, administered by the American Chemical Society, and the Wisconsin Alumni Research Foundation for financial support.

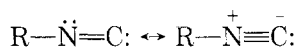
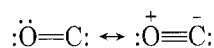
Poly(iminomethylenes): Rigid Rod Helical Polymers

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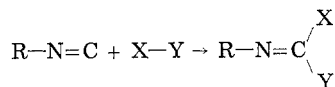
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Isocyanides, also called isonitriles, have an electronic configuration which resembles that of carbon monoxide.



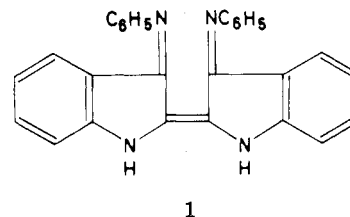
The contribution of the dipolar structure is important, as can be seen from the value of the $\text{N}\equiv\text{C}$ stretching vibration which is in the triple bond region of the infrared, viz. 2100–2200 cm^{-1} . At the same time the carbenic structure of isocyanides is apparent from their ability to give α additions easily.



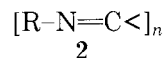
The organic chemistry of isocyanides has been reviewed in several places; refer to the 1971 book edited by Ugi.¹

Ever since Gautier² and Hofmann³ discovered isocyanides in 1867, many authors have noted their tendency to form oligomers and polymers. In only a few cases have these products actually been characterized. For instance, the blue color appearing in phenyl isocyanide at ambient temperature has been proved to be

from the tetramer, indigodianil, 1.⁴



The first reports on polymers of isocyanides are to be found in an article in Japanese by Yamamoto⁵ and in a paper given by Millich⁶ at an ACS meeting. Yamamoto tested the activity of radical initiators, anions, and Lewis acids as catalysts for polymerization. Only Lewis acids, e.g., boron trifluoride, were found to be active. The yields varied from 13 to 45% with an exceptionally high yield of 100% for the polymer of cyclohexyl isocyanide. *tert*-Butyl isocyanide did not polymerize with boron trifluoride but partly oligomerized and partly isomerized to *tert*-butyl cyanide. From spectroscopic data it was suggested that the polymers have structure 2.



(1) I. Ugi, "Isonitrile Chemistry", Academic Press, New York, N.Y., 1971.

(2) A. Gautier, *Justus Liebig's Ann. Chem.*, **142**, 289 (1867).

(3) A. W. Hofmann, *Justus Liebig's Ann. Chem.*, **144**, 114 (1867).

(4) C. Grundmann, *Chem. Ber.*, **91**, 1380 (1958).

(5) Y. Yamamoto, T. Takizawa, and N. Hagihara, *Nippon Kagaku Zasshi*, **87**, 1355 (1966).

(6) F. Millich and R. G. Sinclair, Abstracts, 150th National Meeting of the American Chemical Society, Atlantic City, N.J., Sept 1965. For an historical account, see F. Millich, "Encyclopedia of Polymer Science and Technology", Supplement, Vol. 15, H. Mark, N. G. Gaylord, and N. M. Bikales, Eds., Wiley-Interscience, New York, N.Y., 1971, p 395.

Wieneldt Drenth was born in Groningen, The Netherlands, in 1925. He received his Ph.D. degree with E. H. Wiebenga on X-ray structure determinations of α,ω -diphenylpolyenes. He then switched to physical organic chemistry, and gained experience in working with S. Winstein, J. F. Arens, and G. J. M. van der Kerk. He is a Professor of Organic Chemistry at the University of Utrecht and editor-in-chief of *Recueil des Travaux Chimiques des Pays-Bas*.

Roeland Nolte was born in 's-Heerenberg, The Netherlands, in 1944. He obtained his Ph.D. degree with Professor Drenth on poly(iminomethylenes).

For the polymerization of α -phenylethyl isocyanide, Millich et al.⁷⁻⁹ developed a catalyst which consisted of a strong acid, a radical initiator, and a glass surface; high molecular weight polymers were obtained.

Isocyanides coordinate to metal ions, in particular transition-metal ions.¹⁰ When a large excess of isocyanide is present, polymerization occurs in the case of some metals. The transition metal acts as the catalytic species. This behavior was first mentioned by Yamamoto et al.⁵ who observed the formation of polymers when cyclohexyl isocyanide was treated with carbonyl complexes of zerovalent nickel and cobalt, such as $\text{Ni}^0(\text{CO})_4$ and $\text{Co}_2(\text{CO})_8$. The polymers thus obtained have the same structure, **2**, as is formed by the catalytic action of boron trifluoride. We have investigated in depth the polymerization of isocyanides with nickel(II) complexes.¹¹⁻¹⁹

Millich²⁰ studied polymer properties of the polyisocyanides such as the relation between viscosity and molecular weight and the configuration of the polymer chain. From viscosity behavior, Debye-Scherrer X-ray pictures, optical rotation data, and molecular models, Millich suggested that the polymers have rigid rod helical structures.

A helix is a chiral species: a right-handed helix (denoted by the *P* of plus) and a left-handed helix (denoted by the *M* of minus) are mirror images of each other, but are not superimposable. Helicity should give rise to optical activity. In our laboratory we^{13,14} found further support for Millich's suggestion; we were able to resolve a *tert*-butyl isocyanide oligomer into fractions with (+) and (-) signs of optical rotation.

Next we asked the question: does the fraction with (+) sign of optical rotation contain the *P* or the *M* helices? A merry-go-round mechanism for the polymerization was proposed according to which isocyanide monomers around nickel are converted to polymer repeating units with minimum movement. This mechanism allowed us to predict which screw sense should be preferred when an optically active isocyanide is polymerized. The chirality of these polymers is one of their most interesting features.

The obvious name "polyisocyanides" does not conform to IUPAC rules for the nomenclature of regular single-strand organic polymers.²¹ The prefix *poly*

should be followed by the name of the constitutional repeating unit which, in this case, is a derivative of an iminomethylene, $\text{R}-\text{N}=\text{C}<$. Therefore we prefer the name "poly(iminomethylenes)".

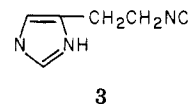
Preparation

Nickel(II) salts have been reported to give unstable and ill-defined substances on reaction with 2 or 4 equiv of isocyanide.²² We have repeated these experiments and found that under properly controlled conditions nickel(II)-isocyanide complexes are in fact stable and can be characterized.^{23,24} However, in the presence of excess isocyanide polymerization occurs, giving poly(iminomethylenes).¹¹

Other metals were also tested for their polymerization activity, but none appeared to be superior to nickel.²⁵ In our opinion, nickel(II)-catalyzed polymerization is the method of choice for preparation of poly(iminomethylenes).

To date, approximately 35 different poly(iminomethylenes) have been synthesized in this way. In a typical experiment a 2 M solution of an isocyanide in methanol is stirred with 1 mol % of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ at 25 °C for 5 h. Under these conditions the yields of polymer amount to 80–100%. Molecular weights are in the range $M_w = 40\,000$ – $60\,000$. Lowering the concentration of catalyst and omission of the solvent can increase the molecular weight up to 150 000.

Isocyanides which have coordinating side groups like carbylhistamine (**3**) are polymerized by nickel chloride

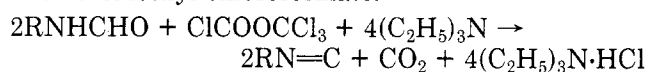


in the presence of 1 equiv of zinc chloride.²⁶ The latter compound blocks the coordinating properties of the imidazole nucleus that otherwise would prevent polymerization.

The heat of polymerization of isocyanides is appreciable, e.g., 81.4 kJ/mol for isopropyl isocyanide.¹⁸ By comparison the heat of polymerization of ethene is 106 kJ/mol.²⁷

Generally, the polymers are soluble in nonpolar solvents and insoluble in polar solvents, except when polar side groups are present.²⁰

The monomeric isocyanides required as starting materials for the polymerization are most easily prepared by dehydration of the corresponding N-substituted formamides.¹ As dehydrating agents we have used phosphorus oxychloride,²⁸ chlorodimethylformiminium chloride (in situ from thionyl chloride and *N,N*-dimethylformamide²⁹), and the recently reported trichloromethyl chloroformate.³⁰



(21) IUPAC, *Pure Appl. Chem.*, **48**, 373 (1976).

(22) L. Malatesta, *Gazz. Chim. Ital.*, **77**, 340 (1947).

(23) R. W. Stephany and W. Drenth, *Recl. Trav. Chim. Pays-Bas*, **91**, 1453 (1972).

(24) R. W. Stephany, R. J. M. Nolte, and W. Drenth, *Recl. Trav. Chim. Pays-Bas*, **92**, 275 (1973).

(25) R. J. M. Nolte, Ph.D. Thesis, Utrecht (1973).

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(27) S. A. Miller, "Ethylene and its Industrial Derivatives", Ernest Benn, London, 1969, p 337.

(28) I. Ugi and R. Meyr, *Chem. Ber.*, **93**, 239 (1960).

(29) H. M. Walborsky and G. E. Niznik, *J. Org. Chem.*, **37**, 187 (1972).

(7) F. Millich and R. G. Sinclair, *J. Polym. Sci., Part C*, **22**, 33 (1968).

(8) F. Millich and R. G. Sinclair, *J. Polym. Sci., Part A-1*, **6**, 1417 (1968).

(9) F. Millich and G. K. Baker, *Macromolecules*, **2**, 122 (1969).

(10) L. Malatesta and F. Bonati, "Isocyanide Complexes of Metals", Wiley, London, 1969.

(11) R. J. M. Nolte, R. W. Stephany and W. Drenth, *Recl. Trav. Chim. Pays-Bas*, **92**, 83 (1973).

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(15) J. M. van der Eijk, R. J. M. Nolte, and W. Drenth, *Recl. Trav. Chim. Pays-Bas*, **97**, 46 (1978).

(16) R. J. M. Nolte, J. A. J. van Zomeren, and J. W. Zwicker, *J. Org. Chem.*, **43**, 1972 (1978).

(17) A. J. Naaktgeboren, R. J. M. Nolte, and W. Drenth, *Recl. Trav. Chim. Pays-Bas*, **97**, 112 (1978).

(18) R. J. M. Nolte, J. W. Zwicker, J. Reedijk, and W. Drenth, *J. Mol. Catal.*, **4**, 423 (1978). Many polymers precipitate during their formation; in these cases the term "initially homogeneous" would be more correct.

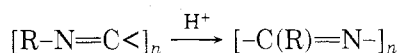
(19) A. J. M. van Beijnen, R. J. M. Nolte, J. W. Zwicker, and W. Drenth, *J. Mol. Catal.*, **4**, 427 (1978).

(20) F. Millich, *Adv. Polym. Sci.*, **19**, 117 (1975); *Chem. Rev.*, **72**, 101 (1972).

One agent might be preferable for one type of isocyanide while another might be better suited for another type of isocyanide. However, trichloromethyl chloroformate seems to be the most versatile.

Configuration

The primary structure of our polymers is that of a poly(Schiff base), $[R-N=C<]_n$. The assignment of this structure is based on elemental analysis and spectral data.^{11,25} The infrared absorption spectra are very similar to those of 1,2-diimines, $[R-N=C(R^1)-]_2$, while the 1H NMR spectrum of a polymer $[R-N=C<]_n$ has its R signals close to those of RNH_2 . Apart from a shoulder at 280 nm, the ultraviolet spectra in chloroform do not show distinct maxima but go upward to lower wavelengths over the region attainable in chloroform. The ultraviolet absorption is much less intense than one would expect for an extended, planar system of sp^2 carbon atoms. In this respect it is worth mentioning that the isomeric polymers of cyanides, $[-C(R)=N-]_n$, are highly absorbing in the ultraviolet and visible region (they are black) and have semi-conducting properties.³¹ These poly(azaethylenes) can be obtained from poly(iminomethylenes) derived from primary alkyl isocyanides by heating or by treatment with a trace of acid.¹¹



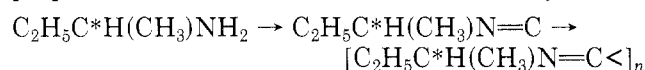
The poly(azaethylenes) can have planar structures, whereas planar space filling models of poly(iminomethylenes) cannot be constructed. Furthermore, the relatively weak UV absorption of poly(iminomethylenes) indicates a nonplanar configuration. Millich⁹ suggested the configuration to be that of a cylindrical helix.

A helical structure would also be anticipated from conformational data on model compounds. Electron diffraction data on the diimine [*t*-BuN=CH-]₂ suggest for the gas phase a dihedral angle around the central C-C bond of 65°. ³² According to electric dipole data the dihedral angle would be even larger in solution.³³ The situation resembles that of vicinal polyketones such as $CH_3(CO)_nCH_3$, for which experimental and theoretical data suggest helical conformations.³⁴ Since there is no steric hindrance to a planar structure, e.g. of $CH_3(CO)_3CH_3$, factors other than steric ones seem to be involved, but they are not yet clearly understood.

Under achiral polymerization conditions our helical compounds should be mixtures of equal numbers of right- and left-handed helices. This view was supported by experiments in which a solution of poly(*tert*-butyliminomethylene) in chloroform was resolved by chromatography on a chiral support into fractions with (+) and (-) signs of optical rotation.¹³ The rotation value could be increased by running the fractions a second time through the column. After three runs a specific rotation $[\alpha]_{578}^{20}$ of 16°, calculated per repeating unit, was obtained.

The support was itself a poly(iminomethylene), viz. poly(*sec*-butyliminomethylene). The latter polymer was

prepared from (*S*)- and also from (*R*)-*sec*-butylamine.



It appeared to be insoluble in chloroform probably because of a high molecular weight.

The question which comes to mind is: which screw sense (*P* or *M*) can be assigned to the molecules in the (+)- and which to those in the (-)-rotating fraction? An answer to this question was obtained by comparing the experimental circular dichroism (CD) spectra with the calculated spectra.¹⁴ According to Tinoco,³⁵ the CD spectrum of a helical polymer can be described by a two-term equation. One term represents the so-called conservative and the other the nonconservative contribution. Both these contributions were calculated as a function of the number of repeating units per turn. The experimental CD curve was also dissected into a conservative and a nonconservative contribution. These experimental contributions could only be fitted to the calculated data when a *P* helix was assigned to the fraction with the (-) sign and an *M* helix to the fraction with the (+) sign of rotation. Moreover, the number of repeating units per turn was confined to the region between 3.6 and 4.6.

This result of approximately four repeating units per turn is in agreement with molecular models. The dihedral angle between two neighboring units is approximately 90° and the height increment per unit 0.1 nm. These numbers may be different for a polymer with substituent R differing from *tert*-butyl. However, the properties of the above-mentioned model compounds, the 1,2-ethanediimines, do suggest that polymers with groups other than R = *tert*-butyl are similarly built.

Does each polymer molecule have the same screw sense over its whole length? This question of whether there are reversals of screw sense in a polymer molecule cannot be answered definitely, but certainly the number of reversals, if any, is low. A reversal of screw sense causes the contributions to the optical activity from the *P* sections of the polymer chain to be compensated by those from the *M* sections. A high number of reversals would lead to a very weak optical activity when the latter is averaged over the repeating units. However, since the experimental and calculated CD spectra are of the same order of magnitude,¹⁴ reversals must at most be few.

A preference for one screw sense can be expected when an isocyanide is polymerized with an optically active nickel complex as the catalyst. Experiments with nickel (L)-alaninate were not successful, probably because of removal of the alaninate from the ligand sphere by excess isocyanide. Experiments with an optically active solvent, viz. *sec*-butyl alcohol, were also unsuccessful. More success was obtained with chiral isocyanides.

When a chiral isocyanide, $R^*N=C$, is polymerized to form $[R^*N=C<]_n$ the polymer molecules with right-handed screw sense are no longer a mirror image of the molecules with left-handed screw sense. Consequently, on polymerization of $R^*N=C$ one of the screw senses will be preferred. Before trying to predict the preferred screw sense let us first consider at which point of its

(30) G. Skorna and I. Ugi, *Angew. Chem.*, **89**, 267 (1977).

(31) D. Wöhrle, *Adv. Polym. Sci.*, **10**, 35 (1972).

(32) I. Hargittai and R. Seip, *Acta Chem. Scand., Ser. A*, **30**, 540 (1976).

(33) O. Exner and J. M. Kligman, *J. Org. Chem.*, **36**, 2014 (1971).

(34) M. B. Rubin, *Chem. Rev.*, **75**, 177 (1975).

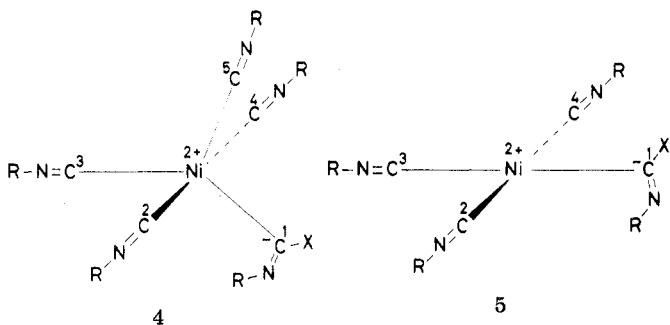
(35) I. Tinoco, *J. Chim. Phys., Phys. Chim. Biol.*, **65**, 91 (1968).

formation the polymer molecule will be coiled into its helical configuration; this could be at the very moment of its birth at the catalytic center or at a later stage. Molecular models show that the latter possibility is unlikely because configurations that differ from the helical one involve so much steric hindrance that they will be almost nonexistent. Knitting the monomers together at the catalytic center in a helical fashion is much more attractive and in agreement with our enantioselective polymerization experiments (*vide infra*). Therefore, in order to know which helical screw sense is induced by a chiral isocyanide, $R^*N=C$, we have to know how the molecules are arranged around the catalytic center.

Polymerization Mechanism

We shall consider the polymerization of isocyanides homogeneously catalyzed by nickel(II) chloride.¹⁸ Addition of an excess of isocyanide to nickel chloride in ethanol initially gives a red solution. A coordination complex cannot be isolated because very soon the polymerization process interferes. However, the spectral characteristics of the red solution are similar to those of the perchlorate $[Ni(CN-t-C_4H_9)_4]^{2+}(ClO_4)_2^-$ which can be isolated and in which the cation has a square-planar structure.²³ Therefore, it will be assumed that square-planar $[Ni(CNR)_4]^{2+}$ is the predominant nickel species under polymerization conditions.

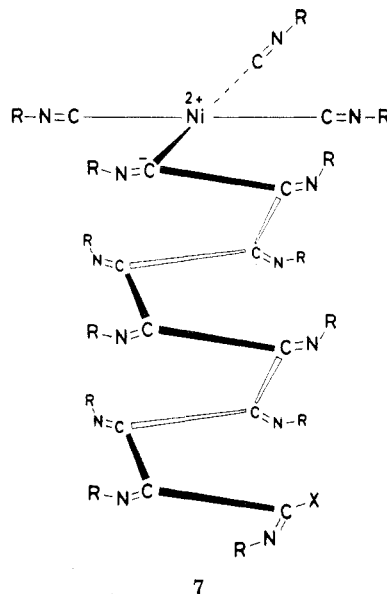
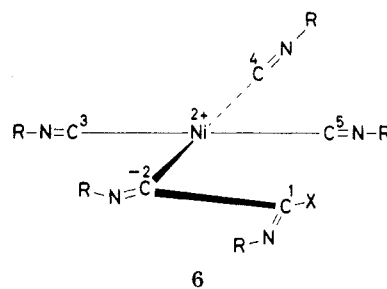
A common reaction of a metal-coordinated isocyanide is nucleophilic attack on its terminal carbon atom.^{36,37} Therefore, a conceivable initiation step of the polymerization is attack on one of the four isocyanide ligands by a nucleophile, giving rise to ion 4 ($X = Cl$ or OC_2H_5



or OH). Structure determinations on similar platinum complexes³⁸ suggest that the plane of the ligand $C(X)=NR$ is approximately perpendicular to the plane of the isocyanide carbons and nickel with R either in the *E* or the *Z* position with respect to X.

In structure 4 carbon atom C^1 has gained considerably in nucleophilicity. As a nucleophile, it is able to attack a neighboring isocyanide carbon. Such an attack is facilitated when a new isocyanide ligand, $C^5=NR$, is substituted for $C^1(X)=NR$. Since substitutions at square-planar nickel are generally of the associative type,³⁹ this substitution is also supposed to be associative; the new ligand enters apically from above and

initially gives rise to the trigonal-bipyramidal intermediate 5. In the rate-determining step C^1 attacks either C^2 or C^4 . When the isocyanide is achiral the attacks on C^2 and C^4 are of equal probability. In 6 the



attack has occurred on C^2 .

Continuing the sequence of attacks, C^1 on C^2 , C^2 on C^3 , etc. in a merry-go-round fashion, the polymer helix grows downwards from the nickel plane. Since one turn of the helix consists of approximately four $RN=C<$ units, each rotation around nickel contributes one turn to the helix. Thus, a stream of monomers enters from above and is transformed into a polymer helix at the slightly wobbling nickel plane.

This mechanism involves a minimal amount of movement and, thus, should involve a relatively low entropy of activation. Indeed, the entropy of activation calculated from the experimental rates of polymerization of isopropyl isocyanide is relatively low,¹² viz. $\Delta S^\ddagger = -54 \pm 13 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, a value which is in the range of the entropies of activation observed for ligand substitutions in square-planar platinum complexes.⁴⁰ The nature of termination is not yet known, but there are several possibilities: blocking of the circular sequence around nickel or attack on the tail carbon of the chain by a proton.

Enantioselective Polymerization

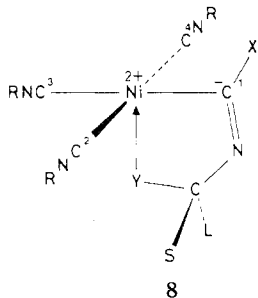
Polymerization of one enantiomer of a chiral isocyanide, $R^*N=C$, gives a polymer whose right- and left-handed helical molecules are not mirror images of each other. They are diastereoisomers and, generally, will not be formed in a 1:1 ratio. Applying our mer-

(36) P. M. Treichel, *Adv. Organomet. Chem.*, 11, 21 (1973).
 (37) Y. Yamamoto and H. Yamazaki, *Coord. Chem. Rev.*, 8, 225 (1972).
 (38) K. P. Wagner, P. M. Treichel, and J. C. Calabrese, *J. Organomet. Chem.*, 71, 299 (1974); E. M. Bradley, K. W. Muir, and G. A. Sim, *J. Chem. Soc., Dalton Trans.*, 1930 (1976); N. M. Butler and J. H. Enemark, *Inorg. Chem.*, 12, 540 (1973).
 (39) F. Basolo and R. G. Pearson, "Mechanism of Inorganic Reactions", Wiley, New York, N. Y., 1967, pp 375 and 417.

(40) Reference 39, p 404.

ry-go-round mechanism, outlined above, we shall derive rules which predict the preferred helical screw sense when we start from an isocyanide, $R^1R^2R^3C-N=C$, where $R^1 \neq R^2 \neq R^3 \neq (N=C)$.

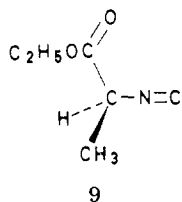
In many of the chiral isocyanides which we subjected to polymerization, one of the R groups, now to be represented by Y, is able to coordinate to nickel(II). For these molecules we suggest the preferred conformation of intermediate 4 to be as in 8, where the two remaining



substituents at the chiral center are distinguished by their relative sizes: S for the smaller and L for the larger substituent. Because the steric hindrance by S is less than by L, in structure 8 C^1 will preferentially attack C^2 . This view is expressed in the following rule: *When in (SYL)C-N=C the substituent Y coordinates to nickel(II), on polymerization a right-handed (P) helix is preferred when in the projection along $\gt C \rightarrow N =$ the sequence $S \rightarrow Y \rightarrow L$ is clockwise and a left-handed (M) helix is preferred when it is counterclockwise.*

We have tested this rule by considering the optical rotation values of a number of polymers obtained from optically active isocyanides of the type (SYL)CN=C.¹⁹ The experimentally observed rotation value is the sum of two contributions: one from the main chain and the other from the side chain. As to the main chain, we generalize the relation we derived for poly(*tert*-butyliminomethylene), viz. a *P* helix gives rise to a (-) sign of optical rotation and an *M* helix to a (+) sign. The side chain, =NR, is, to a large extent, similar to the monomer, C=NR, and therefore we assume the optical rotation contribution by the side chain to be approximately equal to $[\alpha]$ of the monomer.

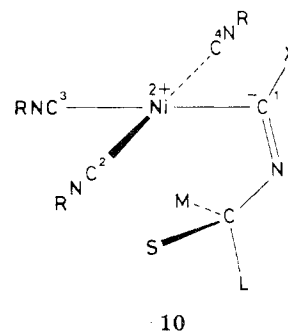
As an example we consider the isocyanide where Y, S, and L are $C_2H_5OC(O)$, H, and CH_3 , respectively. The S enantiomer has the absolute configuration 9. Since



in the projection along the direction $\gt C \rightarrow N =$ the sequence $S \rightarrow Y \rightarrow L$ is clockwise, a right-handed (*P*) screw should be formed. Such a screw would give rise to a (-) sign of optical rotation. Indeed, with respect to the monomer $[\alpha]_{578}^{20}$ of $+16.7^\circ$ the observed polymer $[\alpha]_{578}^{20}$ of -280° (per repeating unit) is highly negative. A positive test of our rule was also obtained for similar molecules with $Y = H_2C=CH$, $HC\equiv C$, C_6H_5 , $C_6H_5CH_2$ and $CH_3C(O)OCH_2$.¹⁹

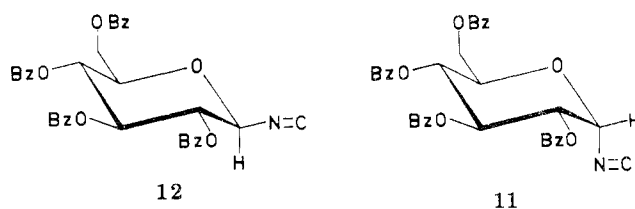
When the chiral center does not carry, apart from the isocyano function, a substituent which is able to co-

ordinate to nickel, the configuration of the first intermediate 4 will probably be as in 10 with the group



C(SML) either in the *E* or the *Z* position with respect to X. The three substituents at the chiral center are distinguished by their sizes: S, M, and L for small, medium, and large. Because of steric effects the L substituent will prefer the *exo* position, while the polymerization will occur on the S side. The corresponding rule says: *Isocyanides (SML)CN=C, in which S, M, and L have no coordinating properties, polymerize preferably to a right-handed (P) helix when in the projection along $\gt C \rightarrow N =$ the sequence $S \rightarrow M \rightarrow L$ is clockwise.*

We are currently investigating the application of this rule to several alkyl isocyanides. Here we mention its application to the polymers of α - and β -D-glucopyranosyl isocyanide (the hydroxyls protected by benzoyl groups), 11 and 12, respectively.¹⁶ Models



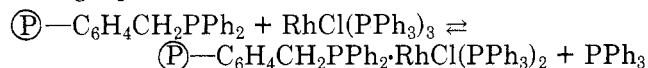
reveal that the bulky benzoyloxy groups allow a configuration of type 10 but prevent the attainment of a configuration of type 8. The rule predicts an *M* and a *P* screw for the α and β anomers, respectively, and thus, a (+) and a (-) contribution to the optical rotation. Indeed, on polymerization of the α anomer the optical rotation of the reacting system increases (from the monomer value of $[\alpha]_{578}^{20} +74.3^\circ$ to the polymer's repeating unit value of $[\alpha]_{578}^{20} > +85^\circ$), whereas with the β anomer the optical rotation decreases (from $[\alpha]_{578}^{20} +46.5^\circ$ to 0°).

The screw sense given by the rules mentioned above could be called "kinetically controlled". When the helix is formed not at the catalytic center but at a later stage, the screw sense would be "thermodynamically controlled". We have derived a rule which predicts the screw sense when it is thermodynamically controlled.¹⁹ When this rule is applied, in several cases disagreement between prediction and experiment occurs. Thus, kinetic control seems to be more likely.

Poly(iminomethylenes) as Catalysts

Anchoring molecules of a homogeneous catalyst to a solid support is a topic of current interest. Such anchoring makes it easy to remove the catalyst by filtration after completion of the reaction. Sometimes anchoring induces higher catalyst activity and greater

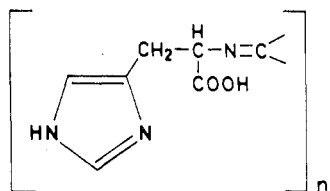
selectivity. Many authors use chloromethylated and slightly cross-linked polystyrene as the supporting polymer, just as Merrifield⁴¹ did in his renowned method for peptide synthesis. For instance, diphenylphosphino groups can be substituted for the chlorine atoms of the polymer and used as ligands for metal ions. Taking Wilkinson's complex as an example, the following equilibrium can be established:



Just like Wilkinson's catalyst, the anchored rhodium complex is active in the hydrogenation of olefins; the anchoring slightly improves the selectivity.⁴²

A polymer-anchored catalyst bears a slight resemblance to an enzyme. Just as in an enzyme, a favorable stereochemistry of the catalytic centers with respect to each other and to the polymer might increase the activity. Polystyrene is a globular polymer in which the environments of the various catalytic centers attached to it are not all the same. Our poly(iminomethylenes) could be a better choice: because of their rigid rod configuration the side chains are in almost identical positions at the rod's surface. Moreover, the chirality of the helices might induce enantioselectivity. So far we have not studied enantioselective catalysis, although we can report on some catalytic reactions.

Detailed results have been obtained for the poly(iminomethylene) **13** derived from L-histidine.¹⁵ Its



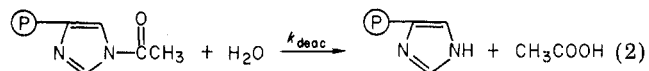
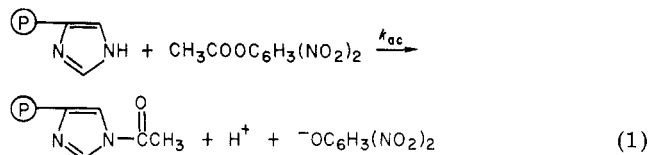
13

catalytic activity⁴³ was investigated for the hydrolysis of 2,4-dinitrophenyl acetate in aqueous solution at pH values ranging from 4 to 10. At each pH the behavior could be analyzed by burst kinetic equations. The "burst" occurs in the initial step and involves rapid acetylation of the catalyst, while an equivalent amount of 2,4-dinitrophenolate ions is released (eq 1). In a subsequent step the catalyst is deacetylated (eq 2). The catalytic activity of the polymer is one to two powers of ten higher than that of L-histidine itself. Such burst

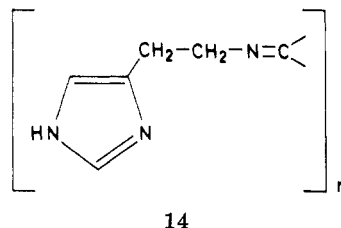
(41) R. B. Merrifield, *Science*, **150**, 178 (1965).

(42) R. H. Grubbs, *Chem. Technol.*, **7**, 512 (1977).

(43) J. M. van der Eijk, Ch. F. Gusdorf, R. J. M. Nolte, and W. Drenth, to be published.

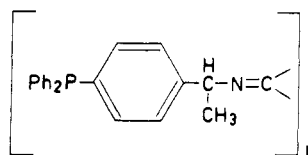


behavior, which is characteristic of a number of enzymatic reactions, was also observed⁴³ for polymer **14**.



14

Another entry to catalysis is by way of polymer **15**.¹⁷



15

By reaction with the Cramer complex $[\text{RhCl}(\text{CH}_2=\text{CH}_2)_2]$ polymers with a rhodium loading varying from 0.2 to 1.0 per polymer unit could be prepared. Preliminary experiments show that this rhodium is catalytically very active in the hydrogenation of olefins.

Concluding Remarks

The pioneering work by Millich and its extensions as to synthesis, configuration, and chirality in our laboratory have established the rigid rod helical character of poly(iminomethylenes). These polymers are now easily available with a large variety of side chains. The combination of chirality and rigidity, with moreover an easy accessibility of the side chains, is attractive for their application in enantioselectivity experiments, e.g., as selective supports in chromatography, as enantioselective catalysts, and as specific reagents with respect to substrates of biochemical importance. With respect to the latter point, we recently observed a very efficient bonding between the bile pigment bilirubin and our imidazole-containing polymer **14**.⁴⁴

(44) R. J. M. Nolte, J. M. van der Eijk, V. E. N. Richters, and W. Drenth, to be published.