Chemical Reviews

THE POLYMERIZATION OF ISOCYANIDES

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Contents

I. Introduction

The field of polymer science abounds in revealing new scientific experiences and is rife with discoveries of challenging phenomena in chemistry, physics, and engineering. Yet, in the present era, the reporting of a successful homopolymerization of a previously untried class of organic compounds with an unsaturated functional group has by now become an infrequent occurrence.

High polymer formation through the agency of the C≡N triple bond, however, has been achieved only lately. The first characterized high polymer of an isocyanide, R—N≡C, and a catalytic synthetic procedure were reported by Millich and Sinclair in 1965.[1] The addition polymerization of acetonitrile, $CH_3C≡N$, to a thermally unstable polymer, by necessity carried out in solid phase, was reported by Kargin in 1961.[2]

As in other notable cases, *e.g.*, polyacrylonitrile, the extreme insolubility of most polyisocyanides presently known has slowed investigation of their syntheses and properties. There have been no polymer applications, although the polymer properties are interesting, and one patent, on poly(cyclohexyl isocyanide), already exists.[8]

Knowledge of self-condensation reactions of isocyanides is in a formative state. It is the purpose of this review to examine those reactions which are relevant to homopolymerization. More generally speaking, the reactions of isocyanide functional groups can lead to some fascinating and valuable examples of multi-bond formation. For instance, condensation reactions frequently incorporate more than one molecule of an isocyanide, producing heterocycles and other interesting compounds.[4] Further, isocyanides can react simultaneously with three other compounds to form complex structures with ease, in high yield, and under mild conditions, as occurs in the Passerini and the Ugi reactions.[5] It is predictable that isocyanides shall find expanding usage in organic and organometallic syntheses.

II. Monomer Properties

Although isocyanides[6] have been known for a century, the chemical literature prior to 1965 shows that exploitation of this class of compounds in syntheses has been sparce. Little detailed attention has been given to mechanistic studies of isocyanide reactions, although they exhibit unique possibilities, since an isocyanide may react as a nucleophile or an electrophile, or may react by a concerted mechanism. Excepting isocyanide isomerization to nitriles, there is also very little quantitative data available concerning isocyanide chemistry. The easy access to isocyanides, provided by fairly recent developments in their preparation, heralds an acceleration in the growth of the chemical literature in this field.

One text devoted to isocyanide chemistry has just appeared,[7] although it failed to treat isocyanide polymerizations. By reference to this convenient monograph a substantial abridgment has been brought about of a previous draft of the present review.

(1) F. Millich and R. G. Sinclair, *Polym. Prepr. Amer. Chem. Soc., Div. Polym. Chem.*, 6, 736 (1965); paper presented at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965; Abstracts, 16th Midwest Chemistry Conference of the American Chemical Society, Kansas City, Mo., Nov 19, 1964, p 30.
(2) V. A. Kargin, V. A. Kabanov, V. P. Zubov, and A. B. Zesin, *Dokl. Akad. Nauk SSSR*, 139, 605 (1961).
(3) R. W. Stackman and W. L. Evers, U. S. Patent 3,423,333 (1969).

(4) B. Zeeh, *Synthesis*, 65 (1969).
(5) I. Ugi in "Newer Methods of Preparative Organic Chemistry," Vol. 4, W. Forest, Ed., Verlag Chemie GmbH, Weinheim/Bergstr., Germany, 1968.
(6) Isocyanides are also known as "isonitriles" and "carbylamines." The last name is not much used, but "isonitriles" is (*cf.* ref 7). "Isocyanides" is the name adopted by IUPAC (*cf.* "Nomenclature of Organic Chemistry," Section C, 1965), and it is currently used in *Chemical Abstracts* indexes.
(7) I. Ugi, Ed., "Isonitrile Chemistry," Academic Press, New York, N. Y., 1971.

A. SOME PHYSICAL PROPERTIES

Isocyanides are compounds in which the multiple bonded functional group may be represented in the ground state by the resonance forms

$$R—\overset{\oplus}{N}\overset{\ominus}{\equiv}C: \longleftrightarrow R—\ddot{N}=C:$$
$$\text{Ia} \qquad\qquad \text{Ib}$$
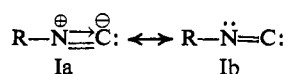
The closest representation of the isocyanide group in the ground state appears to be the cannonical form Ia. This polar form is supported by data from a wide range of physical measurements. It has been suggested[8] that a real difference in structure possibly exists between alkyl and aryl isocyanides, because for the latter a resonance form, $Ar^-=N^+=C:$ (Ic), may be important. The lower infrared absorption frequencies of aryl relative to alkyl isocyanides (by more than 20 cm⁻¹) has been attributed to such resonance. However, the fact that the infrared N≡C stretching frequency of *both* alkyl and aryl isocyanides *similarily* increase with increasing solvent polarity has been interpreted as evidence against appreciable contribution from Ic.[9] Polar solvent apparently enhances the contribution of the polar form Ia.

The electronic structures of a few simple isocyanides only recently have been calculated. Vinyl isocyanide has been examined by means of simple Hückel molecular orbital (HMO) calculations,[10,11] and by means of a full Roothaan self-consistent field (SCF) method.[12] The latter method has also been used for the calculation of methyl isocyanide. Fountain,[13] using an ω' theory,[14-16] has calculated the electronic structure for the isocyanide group in several electronic environments. The charge densities on the nitrogen and carbon atoms (Q_N and Q_C, respectively) and bond orders for the isocyanide groups are summarized in Table I.

The apparent polarity of the isocyanide group is preserved throughout the series of compounds. The strong infrared absorption intensities of isocyanides is due to the considerable charge separation in the functional group.[19] It is interesting to note that by the SCF and the ω' calculations for vinyl isocyanides the polarity difference between the nitrogen and carbon atoms is accentuated, compared to the simple HMO treatment. Ordinarily, the non-iterative HMO method overemphasizes charge separation.[20]

The decrease in bond order of the isocyano group in the two vinyl compounds is indicative of extensive delocalization in these systems. The R–N single bonds joining the isocyano and vinyl groups show the highest π-bond order (*ca.* 0.26) of the six compounds in Table I (*cf.* last column), and the ω'

Table I[13]

π-Charge Distribution about the Isocyano Group of Several Isocyanides, R—N≡C[a]

R	Charge densities of −N≡C		π-Bond orders	
	Q_N	Q_C	N≡C	R—NC
CH₃–[b]	1.475	0.533	1.861	0.180
	(2.855)[c]	(1.147)[c]		
C₆H₅CH₂–	1.475	0.532	1.862	0.176
C₆H₅CH(CH₃)–[d]	1.571	0.430	1.821	0.000
C₆H₅–	1.481	0.520	1.847	0.219
CH₂=CH–	1.648	0.346	1.708	
	(1.20)[e]	(0.80)[e]	(1.91)[e]	0.266
	(1.423)[f]	(0.554)[f]		
CH₂=C(CH₃)–[b]	1.654	0.343	1.704	0.261

[a] Calculations were performed by means of an ω' program, written by K. R. Fountain for the IBM 360/30 (available from Quantum Chemistry Program Exchange, Indiana University, No. 148). The parameters selected were reported by Wohl.[17] [b] Hyperconjugative model for methyl was used. [c] These numbers are gross populations obtained by Clementi and Klint.[12] [d] A non-zero β value is necessary for the inclusion of the saturated (non-hyperconjugating) tertiary carbon atom.[18] A k value of 0.01 was used for the C–CH₃ bond, and a value of 0.007 was used for the C–NC bond. [e] Simple HMO values of Matteson and Bailey.[10] [f] Net populations for 2p$_z$ orbitals.[12]

method produces values of π-bond order of 0.954 and 0.915 for the olefinic bond of the vinyl and isopropylidene groups, respectively. The π-charge densities at the terminal and internal olefinic carbons are 1.125 and 0.881, respectively, in vinyl isocyanide, and 1.182 and 0.839 in isopropenyl isocyanide.

The relative constancy of the π-charge distribution in the isocyano group for the other four isocyanides, methyl through phenyl, is surprising. This suggests that the isocyanide group does not strongly interact with the benzene ring in phenyl isocyanide. The reaction rate of the unimolecular, first-order thermal isomerization is not much affected by variations of the para substituents in aryl isocyanides. This fact might relate only to rotational and vibrationally excited states in which bond order has been decreased or altered by thermal energy. However, one may also consider that the infrared absorption frequencies of various tetrakis(para-substituted phenylisocyano)nickel(0) complexes vary very little with change in the nature of the substituent.[21] The ω' computations show that the π-bond order of the single bond joining the isocyano and vinyl groups is 0.219, showing some amount of π-bond character; and the carbon atoms of the phenyl ring show the following π-charge densities: (C₁) 0.908, (C₂, C₆) 1.047, (C₃, C₅) 0.986, (C₄) 1.027. Thus, the cannonical form Ic is a reasonable but not a major cannonical form.

The triple-bonded functional group in the "Langmuir"[22] form Ia necessarily implies that the ground state for isocyanides is a singlet state, whereas the less polar structure of the "Nef"[23] form Ib would be isomeric with the diradical of the triplet state, an interesting undescribed polar carbene.

(8) L. Malatesta and F. Bonati, "Isocyanide Complexes of Metals," Wiley-Interscience, New York, N. Y., 1969.

(9) W. D. Horrocks and R. H. Mann, *Spectrochim. Acta*, 19, 1375 (1963).

(10) D. S. Matteson and R. A. Bailey, *J. Amer. Chem. Soc.*, 90, 3761 (1968).

(11) D. S. Matteson and R. A. Bailey, *Chem. Ind. (London)*, 191 (1967).

(12) E. Clementi and D. Klint, *J. Chem. Phys.*, 50, 4899 (1969).

(13) Private communication, K. R. Fountain, Chemistry Department, Wisconsin State University, LaCross, Wis. 54601.

(14) A. Streitwieser, Jr., A. Heller, and M. Feldman, *J. Phys. Chem.*, 68, 1224 (1964).

(15) M. Schaley and D. Heidrich, *Monatsh. Chem.*, 99, 588 (1968).

(16) C. A. Coulson and F. Wille, *Tetrahedron*, 22, 3549 (1960).

(17) A. J. Wohl, *ibid.*, 24, 6889 (1968).

(18) A. Streitwieser, *J. Amer. Chem. Soc.*, 82, 4123 (1960).

(19) R. G. Gillis and J. L. Occolowitz, *Spectrochim. Acta*, 19, 873 (1963).

(20) L. Salem, "Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, New York, N. Y., 1960, pp 131–134.

(21) W. Z. Heldt, *Advan. Chem. Ser.*, No. 37, 99 (1963).

(22) The polar structure was proposed by H. Lindemann and L. Wiegrebe, *Chem. Ber.*, 63, 1650 (1930), in analogy with I. Langmuir's postulation in 1919 of the structure of carbon monoxide.

(23) The double bonded structure Ib is one of two proposed originally by A. Gautier, *Justus Liebigs Ann. Chem.*, 146, 119 (1868), and later favored by J. U. Nef, *ibid.*, 270, 267 (1892), and later papers.

The magnitude of the energy difference between the singlet ground state and that of a diradical is not known. Although isocyanides do react with sulfur, selenium, and certain transition metals, *tert*-butyl isocyanide has no effect upon a silver mirror at 80°.[1] Unpaired electrons are observable by some instrumental physical methods (*e.g.*, electron paramagnetic resonance and magnetic susceptibility measurements), but such studies have not been conducted for the purpose of discovering conditions by which isocyanide diradicals exist.

Compared to nitriles, isocyanides are substantially more volatile, absorb at lower infrared frequencies (*ca.* 100 cm^{-1}) with markedly greater intensities, and are easily distinguishable by their vile odors. Isocyanides, being isoelectronic with carbon monoxide, are potentially toxic to mammals, but only a few, *e.g.*, 1,4-diisocyanobutane, are known to exhibit appreciable toxicity to mammals (*cf.* ref 7, p 2, footnote). Boiling and melting points and some spectral data can be found for most known isocyanides in one of two tabulations.[8,24] Ultraviolet spectra of aryl isocyanides are illustrated in another publication.[25]

B. SOME CHEMICAL PROPERTIES

The chemistry of isocyanides that is relevant to polymerization systems is briefly reviewed here to provide a reference background.

Carbon monoxide and isocyanides are the only known stable carbenes. Several isocyanides have been noted to yield with time solid products of self-addition at room temperature, especially when stored neat, as liquids, or in concentrated solutions. A study of ethyl isocyanide at different temperatures describes the following sequence of changes.[26]
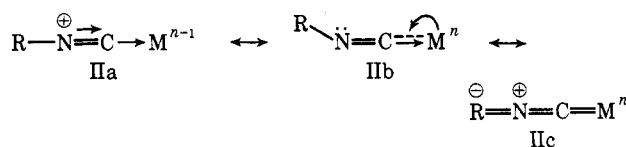
$$\text{isocyanide} \xrightarrow{100°} \text{trimer} \xrightarrow{160°} \text{nitrile}$$
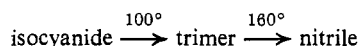
Thermal rearrangement of isocyanides to nitriles, usually at temperatures above 180°, is a general reaction of the class.[26-40]

Very few free-radical reactions of isocyanides are known.[27] Isocyanides are strong reducing agents. Several reports describe isocyanides to be free radical inhibitors,[11,41] yet dibenzoyl peroxide has been reported to give an α,α-addition

product with cyclohexyl isocyanide,[42] and the sulfuric acid catalyzed homopolymerization of α-phenylethyl isocyanide is promoted by oxygen.[1,43]

On oxidation with mercuric oxide, isocyanides are converted into isocyanates. Heated with elemental sulfur, isocyanides will form isothiocyanates. Simple isocyanides add two halogens forming low melting solids of the molecular formula $RNCX_2$, although aliphatic isocyanides (*i.e.*, $>C_{11}$) are reported to form dimeric or trimeric water soluble products of the formula RNCX.[44]

The most common reaction of isocyanides with metals and their compounds is the formation of coordination complexes.[8,45,46] Bond formation of metal *to carbon* is commonly the only alternative that is considered. The presence of the lone electron pair on the carbon atom enables an isocyanide to act as a σ-donor ligand in coordination compounds. Such bonding is commonly represented by the cannonical form IIa. The dative σ bond predictably has considerable ionic character,

$$R\overset{\oplus}{-}\vec{N}\overset{=}{=}C \rightarrow M^{n-1} \quad \longleftrightarrow \quad R\diagdown\overset{\cdot\cdot}{N}=C\overset{\frown}{\Longrightarrow}M^{n} \quad \longleftrightarrow$$
$$\text{IIa} \qquad\qquad\qquad \text{IIb}$$

$$R\overset{\ominus}{=}\overset{\oplus}{N}=C=M^{n}$$
$$\text{IIc}$$

(n = valence of the metal, M)

and its stability must increase with the charge/radius ratio. This type of bonding is characterized by a shift of the isocyanide stretching band in the infrared spectrum to higher frequency upon complex formation; the electropositive field of the metal ion delocalizes the negative charge on the carbon atom of form Ia, resulting in a tightening of the $N{\equiv}C$ triple bond.

However, an isocyanide ligand, having a donor carbon atom of low electronegativity and a potentially vacant orbital, may also act as a π acceptor of electrons with those elements also capable of back-donating electrons, as is shown in form IIb. This type of bonding occurs preferably with transition metals by back-donation of the inner d electrons of the metal to vacant orbitals of the ligand. Coordination compounds of this class are particularly stable when the central atom is in a low valence state. This back-donation usually is only partial. The lessening of the bond order of the $N{\equiv}C$ triple bond is manifested by a bathochromic shift of the infrared stretching frequency, which may exceed in magnitude (depending of the valence of the central element) the hypsochromic effect of the σ-bond formation.[47]

The resonance of form IIc is presumed to occur with some complexed aryl isocyanides accepting back-donation of electrons. Comparison of infrared $N{\equiv}C$ stretching frequencies of complexes is cited as evidence for this phenomenon, since an aliphatic isocyanide ligand would be expected to be a poorer π acceptor and show a higher frequency absorption than its corresponding aryl isocyanide complex.

(24) I. Ugi, U. Fetzer, U. Eholzer, H. Knupfer, and K. Offermann, *Angew. Chem. Int. Ed. Engl.*, **4**, 472 (1965).

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

(26) H. Guillemard, *Ann. Chim.*, [8] **14**, 348 (1908).

(27) T. Saegusa and Y. Ito, *Yuki Gosei Kagaku Kyokai Shi*, **26**, 862 (1968).

(28) A. Gautier, *Ann. Chem. Pharm.*, **146**, 119 (1868).

(29) W. Weith, *Chem. Ber.*, **6**, 212 (1873).

(30) A. W. Hofmann, *ibid.*, **17**, 1914 (1884).

(31) O. Jacobsen, *ibid.*, **22**, 1222 (1889).

(32) J. U. Nef, *Justus Liebigs Ann. Chem.*, **280**, 296 (1894).

(33) G. Kolhmeier and B. S. Rabinovitch, *J. Phys. Chem.*, **63**, 1793 (1959).

(34) S. M. Katzman, M.S. Thesis, University of Missouri-Kansas City, 1962.

(35) F. W. Schneider and B. S. Rabinovitch, *J. Amer. Chem. Soc.*, **84**, 4215 (1962).

(36) J. Casanova, Jr., N. D. Werner, and R. E. Schuster, *J. Org. Chem.*, **31**, 3473 (1966).

(37) S. M. Katzman, Ph.D. Thesis, University of Missouri-Kansas City, 1966, p 53.

(38) S. Yamada, K. Takashima, T. Sato, and S. Terashima, *Chem. Commun.*, 811 (1969).

(39) M. Talat-Erben, E. Uenseren, and N. Seber, *Nucl. Sci. Abstr.*, **19**, 5812 (1965).

(40) R. W. Horobin, N. R. Khan, J. McKenna, and B. G. Hutley, *Tetrahedron Lett.*, 5087 (1966).

(41) R. W. Stackman, *J. Macromol. Sci. Chem.*, **2**, 225 (1968).

(42) R. Oda and T. Shono, *Yuki Gosei Kagaku Kyokai Shi*, **22**, 33 (1968).

(43) For other radical reactions of isonitriles, see T. Saegusa and Y. Ito, *Kagaku No Ryoiki*, **23**, 930 (1969).

(44) E. Jungerman and F. W. Smith, *J. Amer. Oil Chem. Soc.*, **36**, 388 (1959).

(45) F. Klages and K. Mönkemeyer, *Chem. Ber.*, **85**, 126 (1952).

(46) L. Malatesta, *Progr. Inorg. Chem.*, **1**, 283 (1959).

(47) F. A. Cotton and F. Zingales, *J. Amer. Chem. Soc.*, **83**, 351 (1961).

Isocyanide compounds of lanthanides and the following metals have been described.

Ib	IIb	VIa	VIIa		VIII	
Cu	Zn	Cr	Mn	Fe	Co	Ni
Ag	Cd	Mo	...	Ru	Rh	Pd
Au	Hg	W	Re	...	Ir	Pt

Few of the elements of groups Ia–Va show any tendency to form complexes with isocyanides. A few examples are compounds of boron and of aluminum, in which the isocyanide serves solely as a good σ donor.

The metal ions of groups Ib and IIb, each with complete ten-electron d shells, display the usual oxidation states in their isocyanide complexes, and the ligands act as σ donors. In group Ib the affinity toward isocyanides is generally strong and increases with atomic number. Among the Zn-, Cd-, and Hg–isocyanide complexes there is little π-bonding in the ionic carbon–metal bond, and the complexes are rather unstable.

The transition elements of groups VI, VII, and VIII generally form more than one type of isocyanide derivative, corresponding to different oxidation states, the lower oxidation states being the most typical.[8] In general, the compounds are formed of covalent bonds (involving orbitals of the ultimate and often the penultimate electron shells of the central atom) with some double character (as a result of back-donation of d electrons and the π-acceptor function of the ligand). The stability, properties, and structure of these compounds vary greatly with the valence state of the central atom. Ni and Cr, for example, in their zero valence states, and divalent Fe and Pt form very stable complexes.[21, 48]

Isocyanides are stable to alkalies under mild conditions, except for CH_3NC, although a limited number of reports have shown the isocyano group to react with bases (e.g., sodium ethoxide, aqueous hydroxide, and Grignard reagents).[49] The reaction of n-butyllithium with cyclohexyl and phenyl isocyanides at $0°$ in n-hexane gives an α,α-adduct, $RN{=}C$-(Li)C_4H_9.[49a] Dimers, relatively stable allylic anions, also form as the concentration of isocyanide is increased. With p-tolyl isocyanide, hydrogen abstraction from the p-methyl group competes with the α,α-addition. With o- and p-isocyanostyrenes, the addition of butyllithium occurs preferentially at the vinyl group to give a carbanion which is capable of initiating the anionic polymerization of methyl methacrylate, but not of styrene, p-chlorostyrene, or either isocyanostyrene.[49a]

By far the greatest reactivity observed for isocyanides is reaction of the functional group with acidic reactants and catalysts. A general feature of isocyanide reactions is the formation of α,α-addition products; i.e., two new bonds are formed with the terminal isocyano carbon atom. Typical examples include the reaction of isocyanides with Cl_2, O_3, S, Se, and notably with protonic acids. This thermodynamically favorable reaction pattern is not restricted to—nor is it evidence of—an ionic mechanism. In many cases, products are obtained which may be formulated as having been derived from an α,α-addition intermediate by subsequent rearrange-

ments or secondary reactions. The following equations give examples of this formalized pathway.

$$(1)$$

$$(2)$$

$$(3)$$
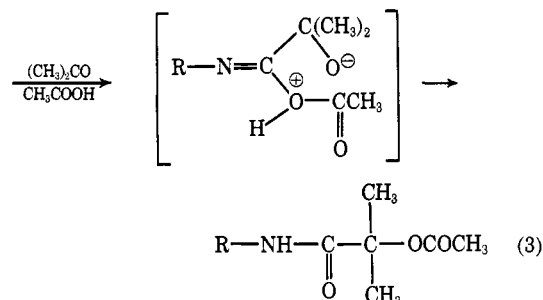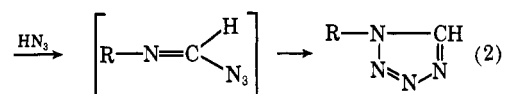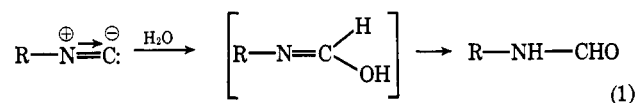
There is a tendency in the literature to classify isocyanide reactions as nucleophilic in nature; however, this is too broad a generalization, and a number of reactions have been reported in which isocyanides act electrophilically, resembling reactions typical for divalent carbon species.[50] When the elements of a protonic acid, HA, add to the terminal carbon, it is plausible that the attachment of a proton to the electrons of carbon (rather than nitrogen) is a first step, for the reason that the C–H bond formation will usually be the most exothermic step in the sequence. However, this need not be true for the action of other Lewis acids and bases; furthermore, in some reactions the addition may be concerted, and thus be independent of the previous ergonic consideration.

Aromatic substitutions of aryl isocyanides can be brought about under harsh conditions, in spite of the great sensitivity of the isocyanide group to acids. This is achieved by the ploy of reacting stable isocyanide complexes.[51,52] Thus, cyanopentakis(benzylisocyano)iron(II) bromide undergoes hydroxymethylation with paraformaldehyde in concentrated sulfuric acid, sulfonation with 20% oleum, bromination with bromine in acetic acid, and nitration with nitric–sulfuric mixed acids.[21] The position of substitution was found to be predominantly or exclusively para, in spite of what may be anticipated from the resonance forms, especially form IIa.
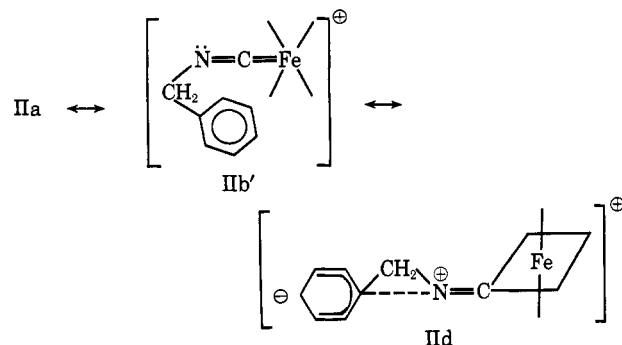
(48) W. D. Becker, W. Beck, and R. Rieck, Z. Naturforsch. B, 25, 1332 (1970).
(49) H. Gilman, "Organic Chemistry," Vol. 2, 2nd ed, Wiley, New York, N. Y., 1947, p 1907.
(49a) G. Smets, L. Andiaenssens, R. van Ael, and P. Caluwe, Makromol. Chem., 145, 149 (1971).

(50) P. Caluwe, Ph.D. Thesis, Leuven, Belgium, 1967.
(51) W. Z. Heldt, J. Org. Chem., 27, 2604 (1962).
(52) W. Z. Heldt, J. Inorg. Nucl. Chem., 24, 73 (1962).

One would also anticipate a very slow rate of electrophilic substitution; instead, in competition reactions the rate of nitration of the first benzylic ligand of the complex was found to be 300-fold faster than benzene, and comparable to the nitration of p-chlorophenol. The results were rationalized as being due to a powerful anchimeric effect, illustrated by IId (and related resonance forms).
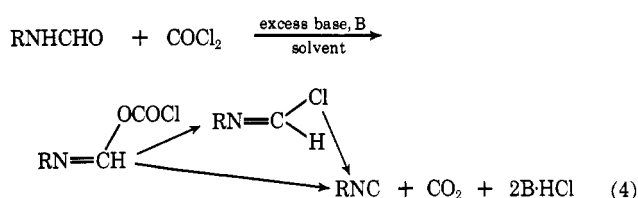
A wide range of chemical reactions of isocyanides can be found discussed in a number of interesting reveiws.[4,5,7,8,43,44,53–56]

III. Important Methods of Monomer Preparation

Various types of reactions leading to isocyanides have been cataloged in a few reference sources.[5,7,24,57,58] In this review, reference is made to the most probably used synthetic routes, and to those which, although not yet fully developed, are promising by virtue of the availability of starting materials or the favorable yields obtained. The following methods have made available not only the simple isocyanides, but also difunctional isocyanides. Thus, diisocyanides, α,β-unsaturated isocyanides, dialkylamino,[59] β-halo, β-hydroxy, and β-keto isocyanides,[60] and α-isocyanocarboxylic esters[61] are known.

A. FROM AMINES AND AMINE DERIVATIVES

The most convenient, general access to isocyanides presently developed is achieved by synthesis starting with primary amines, followed by conversion to N-formamides, and subsequent anhydration as shown in reaction 4.[24] The forma-
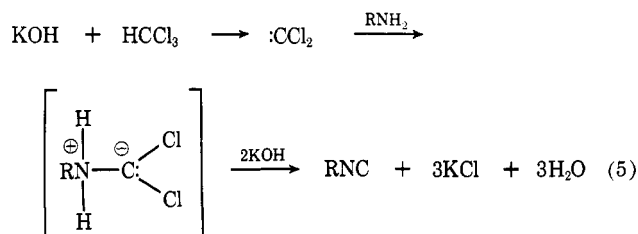
$$RNHCHO + COCl_2 \xrightarrow[\text{solvent}]{\text{excess base, B}}$$

$$RN{=}CH \xrightarrow{OCOCl} RN{=}C\begin{smallmatrix}Cl\\[2pt]H\end{smallmatrix} \longrightarrow RNC + CO_2 + 2B{\cdot}HCl \quad (4)$$

mides are conveniently prepared in good yields from the corresponding available amines by one of several methods.[62–66] Anhydrating agents other than phosgene have been used;[5,24] but in the opinion of the author, phosgene gives the best results, generally, and arylsulfonyl chlorides[67,68] are often inferior. Phosphorus oxychloride (in conjunction

with potassium tert-butoxide) is recommended for the preparation of most alkyl and some aryl isocyanides;[24] it can be used with less danger to the chemist than phosgene portends, especially in large-scale operation. Very mild reaction conditions may make the use of cyanuric chloride preferable in some cases.[69] An excess of tertiary amine is most often used to promote the α,α-elimination from the imine chloride intermediate and to consume the hydrogen halide which is generated. The particular amine used is chosen on the basis of its ease of drying and by consideration of its reflux temperature or dissimilarity of boiling point to that of the product isocyanide. For cases in which the α,α-elimination is sometimes difficult, other bases have been used, e.g., alkaline carbonates, potassium tert-butoxide, and liquid ammonia. Methylene chloride and other halogenated hydrocarbons are often the solvents of choice. The related N-monosubstituted thioformamides give the same reaction,[70] and aldoximes have been similarly anhydrated with p-toluenesulfonyl chloride.[71,72]

Fewer than 40 organo isocyanides were described in the chemical literature prior to 1965, when Ugi and coworkers first reported 242 isocyanides prepared by modifications of the above reaction with phosgene.[24]

The Hofmann "carbylamine" reaction, discovered contemporaneously with Gautier's first isocyanide syntheses, also depends on the availability of appropriate primary amines as starting materials, and it has most often been used to prepare aryl isocyanides. Dichlorocarbene is generated in situ from the reaction of hydroxide ion and chloroform, which then attacks the amine as shown in eq 5. Quite

$$KOH + HCCl_3 \longrightarrow :CCl_2 \xrightarrow{RNH_2}$$

$$\begin{bmatrix} H \\ \overset{\oplus}{|} \quad \ominus \\ RN{-}C{:} \xrightarrow{} \overset{Cl}{\underset{Cl}{\diagup}} \\ | \\ H \end{bmatrix} \xrightarrow{2KOH} RNC + 3KCl + 3H_2O \quad (5)$$

often the yields are modest, and the reaction is many times attended by tarry byproducts. To minimize these features, a procedure has been published in which the chloroform reagent is added dropwise at ice-bath temperature over a period of 30 min to a solution of the primary amine and sodium tert-butoxide in hexane or toluene–hexane.[73] Yields ranged from 71 to 98% in the preparation of five aryl isocyanides.

B. ALKYLATION OF METAL CYANIDES

In 1866–1869, Gautier reported the preparation of methyl, ethyl, and isopropyl isocyanides by the reaction of silver cyanide with alkyl iodides (eq 6).[74–79] Reaction inter-

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(66) S. Sugasawa and H. Shigehara, J. Pharm. Soc. Jap., **62**, 531 (1942).
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(73) T. Shingaki and M. Takebayashi, Bull. Chem. Soc. Jap., **36**, 617 (1963).
(74) A. Gautier, C. R. Acad. Sci., **63**, 93 (1866).
(75) A. Gautier, Justus Liebigs Ann. Chem., **142**, 289 (1867).
(76) A. Gautier, ibid., **146**, 119 (1868).
(77) A. Gautier, ibid., **149**, 29, 155 (1869).
(78) A. Gautier, ibid., **151**, 239 (1869).
(79) A. Gautier, Ann. Chim., (4) **17**, 103, 203 (1869).

$$RX + (CN-Ag)_x \longrightarrow RCN + RNC-AgX \xrightarrow{KCN}$$
$$RCN + RNC + KAg(CN)_2 \quad (6)$$

mediates, e.g., $(AgCN)_2 \cdot RX$ and $AgCN \cdot RX$, have been suggested.[80] Mixtures of nitriles and isocyanides are produced, the more stable nitriles predominating at higher temperatures.[81] Cuprous cyanide has also been used analogously, accompanied by the formation of intermediate coordination compounds, but the yields of the isocyanides are usually lower.[82] Active alkyl or aryl halides,[48] alkyl sulfate,[83] diazomethane,[84] and even organometallic halides[85] have been used as alkylating agents. Several of these types of alkylating agents have been used to alkylate ferrocyanides.[21]

A very recent modification of this reaction, prior to treatment with alkyl halide, involves the reaction of silver cyanide with tetraphenylarsonium halide or triphenylmethylphosphonium halide to produce an onium dicyanoargentate.[86] These reagents give homogeneous solutions for the reaction in dipolar aprotic solvents. Impressive yields were obtained for the preparation of methyl (80%) and benzhydryl isocyanides (88%).

Tertiary alkyl isocyanides can now be prepared, apparently free of the isomeric nitriles, by N-alkylation of HCN with unsymmetrical disubstituted olefins in the presence of cuprous bromide.[87] The products show Markovnikov addition of HNC. In general, the olefin, HCN, and CuBr are mixed in molar ratio of 4:4:1 and heated at 100°, at autogenous pressure, for 5 hr or more. Complexes of the type $(RNC)_3CuBr$ and $(RNC)CuCN$ are formed, from which the tertiary isocyanide is liberated with aqueous KCN. The amount of the cuprous halide used may be reduced beneficially, and, it was mentioned, it may be used in catalytic amount under proper conditions. The yields range from 0.8 to 1.7 mol/g-atom of Cu, for a wide range of disubstituted mono- and diolefins. Ethylene, propylene, 1- and 2-butenes, and butadiene failed to react at temperature below 100°, while isoprene and 2,3-dimethylbutadiene give mixtures of nitriles and isocyanides.

C. DECHALCONIZATION OF ISOCYANATES AND ISOTHIOCYANATES

Isocyanates and isothiocyanates are obtainable through a number of synthesis routes from more commonly available compounds (e.g., amines or alkyl halides), and also from urethanes and acyl azides. In most cases, the preparation of isocyanides via the corresponding isocyanate would be less direct than by one of the isocyanide syntheses described above. However, some isocyanates are commercially available, and some recently reported methods of the dechalconization of reactions have claims of good yields.

The treatment of isocyanates with triethyl phosphite at temperatures above 150° affords several isocyanides in

yields of 20-57%.[88] Isothiocyanates may also be used.[89] It is not surprising that at the elevated temperatures often employed the thermal rearrangement product of an isocyanide, i.e., the corresponding nitrile, is often isolated, sometimes exclusively. More recently, triethyl phosphite has been replaced by 2-phenyl-3-methyl-1,3,2-oxazaphospholidine, which is prepared from 2-methylaminoethanol and phenylphosphonous dichloride or phenylbis(diethylamino)phosphine.[90] It was found to react with isocyanates or isothiocyanates at low temperatures (5-36°) as shown in eq 7.
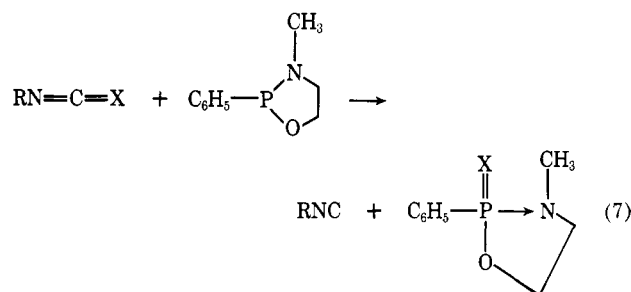
Yields of 51-93% were obtained for ethyl, phenyl, o-tolyl, and p-chlorophenyl isocyanides in preparations beginning with isocyanates or isothiocyanates, the latter providing better yields.

Other dechalconizing agents which have been employed include methyllithium,[24] triphenyltin hydride,[91] and copper,[92] and ultraviolet radiation, in the case of the generation of transient methylethoxycarbene from O-ethyl thioacetate,[93] and of o-biphenyl isocyanide from its corresponding isothiocyanate.[94]

D. ALKYLATION OF α-ISOCYANOALKANOIC ESTERS

Most monomer preparations involve the generation of the isocyano functional group. A valuable adjunct to these reactions is one in which the residue of an isocyanide can be modified. In analogy with the malonic ester and the acetoacetic ester chain-lengthening syntheses, α-isocyanoacetic and α-isocyanopropionic esters can be α-metalated in the presence of tert-C_4H_9OK or NaH in tetrahydrofuran or ether-DMSO. The subsequent addition of alkylating agents, e.g., alkyl halides, gives impressive yields.[94a] Dialkylated isocyanoacetic esters can easily be obtained from ethyl isocyanoacetate and 2 equiv of alkylating agent. Both 1,2-dibromoethane and 2-chloroethyl p-toluenesulfonate react with ring closure to ethyl 1-isocyanocyclopropanecarboxylate. Monoalkylation of α-isocyanoacetic ester can be obtained from the tert-butyl ester. Considerable preparative importance can be attached to this general approach since the isocyano and the ester groups are easily convertible to a variety of interesting derivatives.

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IV. Polymerizations

A. HISTORY

The tendency of isocyanides to resinify, thermally or in the presence of catalysts, was early suspected to be a property of this chemical class. Thus Gautier observed that methyl isocyanide turns to a white solid of mp 41°,[95] and Nef reported the spontaneous formation of red needles from phenyl isocyanide.[96] Guillemard,[97] Wade,[98] Esafov,[99,100] and Grundmann[101] also isolated crystalline or resinous substances from the storage of purified phenyl isocyanide. Grundmann, for instance, showed his blue material to be tetrameric, i.e., the insoluble indigo-β,β-dianil (III), whereas Esafov reported a dimer.[99] Guillemard concluded, on the basis of cryoscopy, that ethyl isocyanide forms a trimer upon thermal treatment.[81] Passerini proposed, on the basis of cryoscopy, that one of the products found after heating a benzene solution of phenyl isocyanide in the presence of nitrosobenzene had the trimeric structure, 3,4-dianil-3,4-dihydroquinoline (IV).[102]
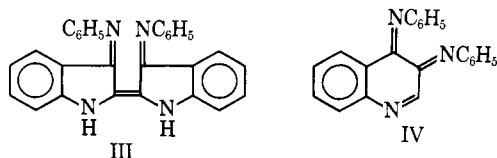
Hammick, et al., synthesized a series of para-substituted phenyl isocyanides and found the following decreasing order of the effect of substituents with respect to the tendency of the compounds to resinify spontaneously to dark green solids of low melting points: Cl > CH_3 > CH_3O.[103] Ugi and Meyr also noted the instabilities of p- and o-chlorophenyl isocyanides, which they said showed discoloration in minutes at room temperature.[25]

Klages and Mönkemeyer reported that boron trifluoride catalyzed the polymerization of p-tolyl isocyanide.[45] The reaction was conducted in absolute ether at −70° followed by the removal of volatile components under vacuum. A brown film adhering to the container walls, easily dissoluble, was designated as polymer, which became brittle after lengthy exposure to air. (Note, however, that the property of easy solubility is not a characteristic of poly(tolyl isocyanides), for which no true solvent has yet been found.) More recent experimental evidence shows that Friedel–Crafts catalysts, such as BF_3, are capable of polymerizing isocyanides. However, without reinvestigation of the product obtained by Klages and Mönkemeyer, it is impossible to know what was the structure or molecular weight of their product.

Oda and Shono mention that cyclohexyl isocyanide yields a "resin-like substance" as the main product of treatment with di-tert-butyl peroxide, although dibenzoyl peroxide gives a simple α,α-addition product.[42] In general,

free radicals have failed to polymerize isocyanides.[1,41,104,105] In fact, isocyanides are claimed to be free-radical inhibitors.[11]

Papenmeier found that m-tolyl isocyanide is very prone to spontaneous "polymerization," yielding a yellow solid which is insoluble in a variety of solvents.[106]

Vinyl isocyanide is described as darkening on irradiation, or during storage at temperatures greater than −15°, whereupon it deposits brown resin on ground-glass surfaces.[11]

All reports of "polymers" or "resins" from isocyanides with the exception of poly(α-phenylethyl isocyanide) have lacked any confirmation of their high polymer nature. The only characterization reported prior to 1965 involved cryoscopy on products soluble in benzene, which showed degrees of polymerization in the range of 2–3.

In 1962, Millich observed the slow deposition of high molecular weight polymer from shelf-stored samples of α-phenylethyl isocyanide and other isocyanides.[1] The products displayed their natural white or yellow color, and the supernatent monomers remained relatively pure. Modern syntheses of polyisocyanides therefore began in 1965 with the report by Millich and Sinclair of a catalytic system for the controlled polymerization of α-phenylethyl isocyanide and the characterization of the high molecular weight product.[1,105,107,108] This polymer and two others, synthesized by Millich and coworkers from β-phenylethyl isocyanide and from dl-methyl α-isocyanoproprionate, are the only presently known soluble homopolymers of isocyanides of high molecular weight.[109] Thus, molecular weight and conformational studies by solution characterization methods are now available for more than one polyisocyanide.

B. OLIGOMERIZATION

Several of the above reactions are distinguished by the tendency of incorporating more than one isocyanide molecule at a time. The formation of compounds III and IV are examples. So is Kabbe's tert-butyl isocyanide dimer,[109a] and Esafov's phenyl isocyanide "dimer,"[99] now considered to be N,N'-diphenylformamidine.[101] Such oligomeric products can result if (a) the reactivity of the primary reaction product is sufficient to attack coexisting free isocyanides or (b) the isocyanide is aggregated to a polymolecular complex prior to reaction. α-Phenylethyl isocyanide, for instance, shows departure from obeyance of the Beer–Lambert law.[108] Adsorption on surfaces or complexation by metal ions may also serve to facilitate a multiple addition reaction.[107] A tendency toward cyclic product formation is one cause of failure against sustaining a polymer chain propagation reaction;[110] other possible causes are not yet fully evident.

Anionic initiators have produced dimers from isocyanides, without polymerization. Butyllithium,[50] butylmagnesium

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(96) J. U. Nef, Justus Liebigs Ann. Chem., 270, 267, 275 (1892).
(97) H. Guillemard, Ann. Chim., [8] 14, 358 (1908).
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(99) V. I. Esafov, J. Gen. Chem. USSR, 14, 299 (1944).
(100) V. I. Esafov, ibid., 17, 1516 (1947).
(101) C. Grundmann, Chem. Ber., 91, 1380 (1958).
(102) M. Passerini and T. Bonciani, Gazz. Chim. Ital., 61, 959 (1931).
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(105) F. Millich and R. G. Sinclair, J. Polymer Sci., Part A-1, 6, 1417 (1968).
(106) G. J. Papenmeier, M.S. Thesis, University of Missouri-Kansas City, 1960.
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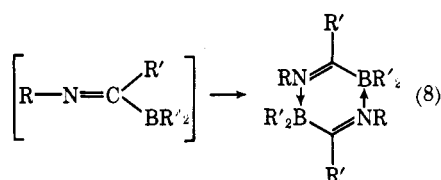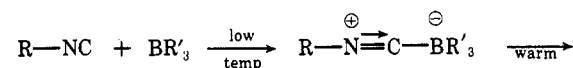(108) F. Millich and G. K. Baker, Macromolecules, 2, 122 (1969).
(109) F. Millich, G-m. Wang, S. Kapur, J. Chenvanij, C. E. Carraher, Jr., and R. G. Sinclair, unpublished results.
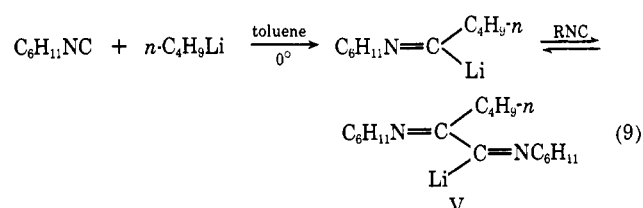(109a) H. J. Kabbe, Angew. Chem., 80, 406 (1968).
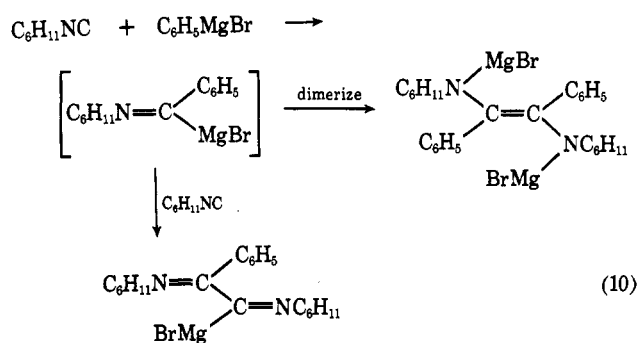(110) G. Gee in "Inorganic Polymers," Special Publication No. 15, The Chemical Society, London, 1961, p 67.

halides,[111] triethylaluminum,[112] trialkylboranes,[113-116] and sodium in ammonia[117] have been tried, as shown in eq 8

$$R{-}NC \ + \ BR'_3 \ \xrightarrow[\text{temp}]{\text{low}} \ R{-}\overset{\oplus}{N}{\equiv}\overset{\ominus}{C}{-}BR'_3 \ \xrightarrow{\text{warm}}$$

$$\left[R{-}N{=}C\overset{R'}{\underset{BR'_2}{\diagup}} \right] \longrightarrow \underset{R'_2B}{\overset{RN}{\diagup}}\underset{NR}{\overset{BR'_2}{\diagdown}}R' \quad (8)$$

$$R = CH_3, C_2H_5, C_6H_5, \textit{tert-}C_4H_9; \ R' = CH_3, C_2H_5$$

$$C_6H_{11}NC \ + \ \textit{n-}C_4H_9Li \ \xrightarrow[0°]{\text{toluene}} \ C_6H_{11}N{=}C\overset{C_4H_9\textit{-n}}{\underset{Li}{\diagup}} \ \xrightleftharpoons{\text{RNC}}$$

$$C_6H_{11}N{=}C\overset{C_4H_9\textit{-n}}{\underset{C{=}NC_6H_{11}}{\diagdown}} \quad (9)$$
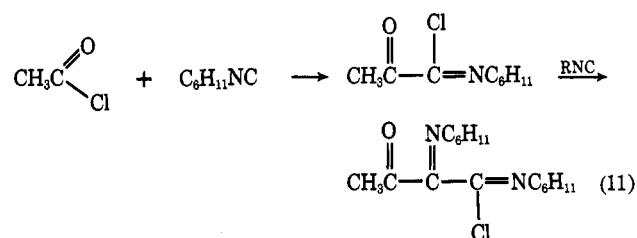
$$\underset{Li}{} \quad V$$

and 9. The product V is an allylic anion and is unreactive toward further isocyanide addition.[49a] Reaction 10 shows greater complexity.[111]

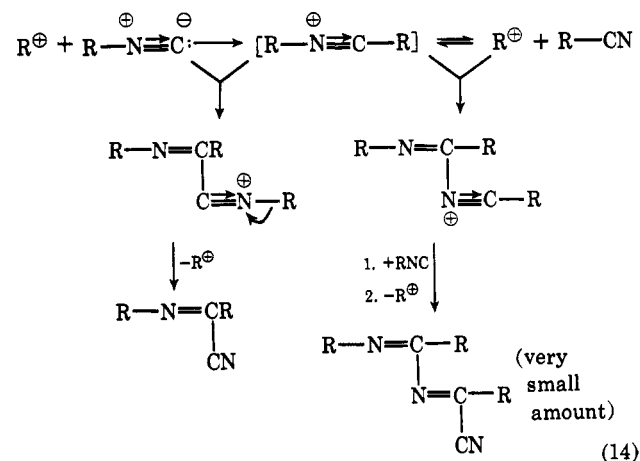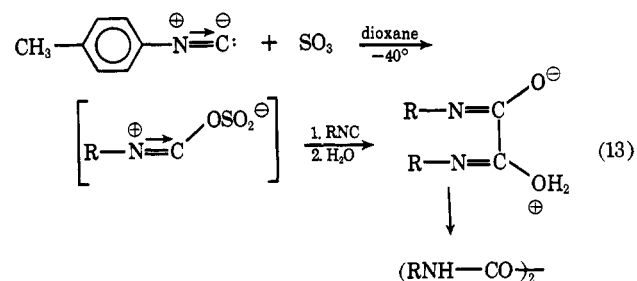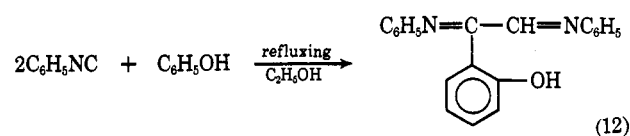$$C_6H_{11}NC \ + \ C_6H_5MgBr \ \longrightarrow$$

$$\left[C_6H_{11}N{=}C\overset{C_6H_5}{\underset{MgBr}{\diagup}} \right] \xrightarrow{\text{dimerize}} \ \underset{C_6H_5}{\overset{C_6H_{11}N}{\diagdown}}\underset{MgBr}{\overset{MgBr}{}}C{=}C\underset{NC_6H_{11}}{\overset{C_6H_5}{}}$$

$$\Big\downarrow C_6H_{11}NC$$

$$C_6H_{11}N{=}C\overset{C_6H_5}{\underset{C{=}NC_6H_{11}}{\diagdown}} \quad (10)$$

$$\underset{BrMg}{}$$

Other examples exist in which another reactant takes part[118-120] (see eq 11-13).

Tertiary alkyl isocyanides, under the action of SnCl₄ or BF₃·O(C₂H₅)₂, undergo oligomerizations[109a] coupled with rearrangements at room temperature and below.[121] Although a primary dissociation to yield some tertiary carbonium ion is called for, the isomerization is pictured as a cleavage of R—⁺N≡C—R, the N-alkylated isocyanide. Cleavage emits the carbonium ion again, the rearranged nitrile product, and dimeric products (eq 14). TiCl₄ and AlCl₃

(111) I. Ugi and U. Fetzer, *Ber.*, **94**, 2239 (1961).

(112) G. Hesse, H. Witte, and P. Mischke, *Angew. Chem., Int. Ed. Engl.,* **4**, 355 (1965).

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(114) J. Casanova, Jr., H. R. Kiefer, D. Kuwada, and A. H. Boulton, *ibid.*, 703 (1965).

(115) S. Bresadola, G. Carraro, C. Pecile, and A. Turco, *ibid.*, 3185 (1964).

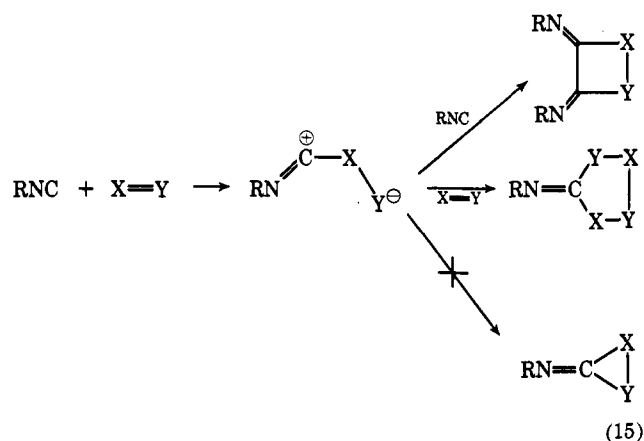(116) G. Hesse, H. Witte, and W. Gulden, *ibid.*, 2707 (1966).

(117) W. Bückner and R. Dufaux, *Helv. Chim. Acta*, **49**, 1145 (1966).

(118) I. Ugi and U. Fetzer, *Ber.*, **94**, 1116 (1961).

(119) M. Passerini, *Gazz. Chim. Ital.*, **54**, 529 (1924).

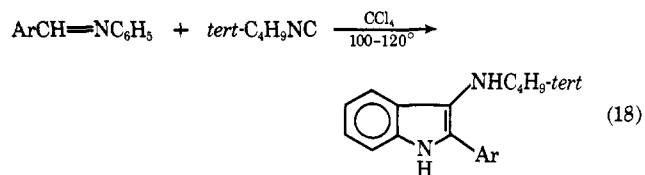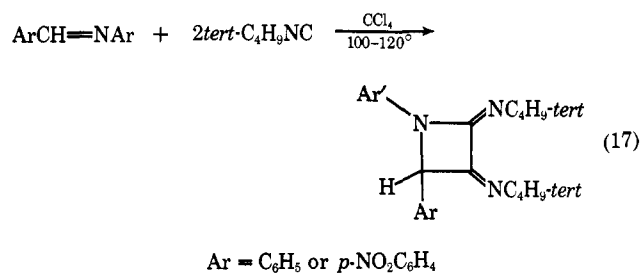(120) F. Klages and K. Mönkemeyer, *Ber.*, **85**, 129 (1952).

(121) T. Saegusa, N. Taka-ishi, and Y. Ito, *J. Org. Chem.*, **34**, 4040 (1969).

$$CH_3C\overset{O}{\underset{Cl}{\diagup}} \ + \ C_6H_{11}NC \ \longrightarrow \ CH_3C\overset{O}{\underset{}{\|}}{-}\overset{Cl}{\underset{}{C}}{=}NC_6H_{11} \ \xrightarrow{\text{RNC}}$$

$$CH_3\overset{O}{\underset{}{C}}{-}\overset{NC_6H_{11}}{\underset{Cl}{C}}{-}C{=}NC_6H_{11} \quad (11)$$

and oligomers

$$2C_6H_5NC \ + \ C_6H_5OH \ \xrightarrow[C_2H_5OH]{\text{refluxing}} \ \underset{}{C_6H_5N{=}C{-}CH{=}NC_6H_5}$$

$$\underset{OH}{} \quad (12)$$

$$CH_3{-}\langle\bigcirc\rangle{-}\overset{\oplus}{N}{\equiv}\overset{\ominus}{C}{:} \ + \ SO_3 \ \xrightarrow[-40°]{\text{dioxane}}$$

$$\left[R{-}\overset{\oplus}{N}{\equiv}\overset{}{C}\overset{}{\underset{OSO_2}{\diagup}}^{\ominus} \right] \ \xrightarrow[2.\,H_2O]{1.\,RNC} \ R{-}N{=}C\overset{O^{\ominus}}{\underset{}{}}$$

$$R{-}N{=}C\overset{}{\underset{\overset{\oplus}{OH_2}}{}} \quad (13)$$

$$\Big\downarrow$$

$$(RNH{-}CO)_2^-$$

$$R^{\oplus} + R{-}\overset{\oplus}{N}{\equiv}\overset{\ominus}{C}{:} \longrightarrow [R{-}\overset{\oplus}{N}{\equiv}C{-}R] \rightleftharpoons R^{\oplus} + R{-}CN$$

$$R{-}N{=}CR \qquad\qquad R{-}N{=}\overset{}{C}{-}R$$
$$\overset{\oplus}{C}{\equiv}N{-}R \qquad\qquad \overset{}{N}{\equiv}\overset{\oplus}{C}{-}R$$

$$\Big\downarrow {-}R^{\oplus} \qquad\qquad \overset{1.\,+RNC}{\underset{2.\,-R^{\oplus}}{\Big\downarrow}}$$

$$R{-}N{=}CR \qquad\qquad R{-}N{=}\overset{}{C}{-}R$$
$$\overset{}{CN} \qquad\qquad \overset{}{N}{=}\overset{}{C}{-}R \quad \begin{array}{l}\text{(very}\\ \text{small}\\ \text{amount)}\end{array}$$
$$\qquad\qquad\qquad \overset{}{CN} \quad (14)$$

$$R = \textit{tert-}C_4H_9, \text{3-methyl-3-pentyl}$$

formed metal complexes with the isocyanides and failed to induce the above reaction.[121]

Addition reactions between isocyanides and double-bond systems, such as C=O, C=N, N=O, and activated C=C functions, have been reviewed recently.[4] These additions generally involve the reaction of three molecules, are catalyzed by boron trifluoride, and, in contrast to the Passerini and Ugi reactions, are carried out in aprotic medium. The reactions are formalized as dipolar cycloadditions, affording four-membered heterocycles (from a 1:2 reaction stoichiometry of double-bond function:isocyanide) and five-membered heterocycles (from a 2:1 stoichiometry), as shown in eq 15.[4] The primary 1:2 reaction products may in many cases be isolated or may be readily converted to other products in which ring opening or rearrangement to five-membered heterocycles has occurred. The formation of larger rings is seldom observed, although it is in principle possible.

Since the first product of addition reaction of an isocyanide produces a Schiff's base, an examination of such dipolar reactions of isocyanides with azomethines is per-

$$RNC + X=Y \longrightarrow RN=\overset{\oplus}{C}\!-\!X \underset{Y^{\ominus}}{\Big\backslash}$$

(15)

tinent to consideration of isocyanide polymerizations. Reactions have been reported in which are formed the 2:1,[122] the 1:2,[123] and also 1:1 products[123] (eq 16).

$$2C_6H_5CH{=}NR + R'NC \xrightarrow[\text{AlCl}_3]{\text{ether, 25°}} \quad (16)$$

R, R' = alkyl
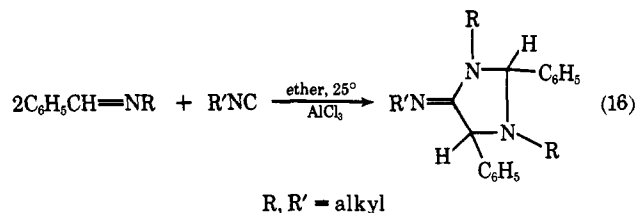
2,5-Diphenylimidazolidines are produced in 80–90% yields if the azomethines are present in very large excess. The 2,3-bis(tert-butylimino)azetidines are favored (51–70%

$$ArCH{=}NAr + 2tert\text{-}C_4H_9NC \xrightarrow[100{-}120°]{CCl_4}$$

(17)

Ar = C₆H₅ or p-NO₂C₆H₄

$$ArCH{=}NC_6H_5 + tert\text{-}C_4H_9NC \xrightarrow[100{-}120°]{CCl_4}$$

(18)

yields) with Schiff's bases from p-nitroaniline, whereas, 3-tert-butylamino-2-phenylindoles result (27–41% yields) as the major products with Schiff's bases from aniline. Reaction 17 was also accomplished at room temperature with trifluoroacetic acid catalysis in nonpolar hydrocarbon medium, and reaction 18 in a hydrochloric acid–carbon tetrachloride mixture, but no reaction was observed under various conditions in polar solvents.

The structures of the azetidines was supported by mass spectral data and proved by hydrolysis. They are found to have characteristic infrared absorptions at 1670 and 1720

cm⁻¹, attributable respectively to conjugated and nonconjugated four-membered ring imine groups.

The self-condensation of isocyanides holds considerable synthetic utility, not only for the preparation of high polymers but also of interesting heterocycles and oligomeric derivatives. The preceding reaction conditions are very similar to some used for the preparation of high polymers. Successful control of syntheses requires additional knowledge of the reaction mechanisms so as to separate polymer formation from conjunct reactions.

C. MODERN SYNTHESES OF POLYISOCYANIDES

Various polyisocyanides have now been reported in the last 6 years.[124] The chemical preparations may be classified among four types: (a) catalysis by protonic acids, with and without promotors; (b) catalysis by certain Lewis acids, principally BF₃; (c) decomposition of metallo–isocyanide complexes; and (d) spontaneous polymerizations and polymerizations in the presence of ground glass. Typical reaction conditions for these systems tend to distinguish them further.

1. Protonic Acid Catalysis

Typically these reactions are conducted in the temperature range 25–100°, in periods of hours or days, and in a medium in which the polymer is insoluble. Sulfuric acid, as a fine droplet dispersion in heptane,[109] or coated on powdered glass,[105] has most often been used. Other catalysts (e.g., H₃PO₄, NaHSO₄, ion-exchange resins in their acid forms) have been substituted for sulfuric acid, but with decreases in the rate of monomer conversion. Strong acids, when used indiscriminantly, generally cause deleterious effects with isocyanides, giving complex mixtures of dark oils or resins which are reminiscent of the product descriptions of past literature.

The rate of polymerization in the best studied case (i.e., α-phenylethyl isocyanide) is promoted by oxygen or peroxides and is not inhibited by 1,4-naphthoquinone or m-dinitrobenzene.[105] The chemical role played by free radical promoters during sulfuric acid catalysis is still an unanswered question. Precise kinetic study of the reaction is hampered by the heterogeneity of the reaction phase and the modest reproducibility of the system; however, the following features have been observed: (a) sigmoidal growth curves are observed for yield as a function of time, which become arrested at various conversions, from 20 to 100%, for as yet undetermined causes; (b) the $\overline{DP}$ increases with time, as the number of polymer molecules and their lengths continue to increase (cf. Figure 1); (c) the amount of sulfuric acid used as a coating on glass passes through a maximum in catalytic efficiency and product molecular weight; (d) molecular weight varies inversely with temperature.[109] The correlating increases of yield and $\overline{DP}$ is more suggestive of a stepwise reaction mechanism than a chain addition mechanism. In contrast, the rapid, low-temperature Lewis acid-catalyzed polymerizations, described below, are probably chain reactions.

The polymerization of α-phenylethyl isocyanide employing sulfuric acid coated ground glass and oxygen shows a

(122) T. Saegusa, N. Taka-ishi, J. Tamura, and H. Fujii, J. Org. Chem., 34, 1145 (1969).
(123) J. A. Deyrup, M. M. Vestling, W. V. Hagan, and M. Y. Yun, Tetrahedron, 25, 1467 (1969).

(124) F. Millich in "Encyclopedia of Polymer Science and Technology," Suppl., Vol. 15, H. F. Mark, N. G. Gaylord, and N. M. Bikales, Ed., Wiley-Interscience, New York, N. Y., in press.
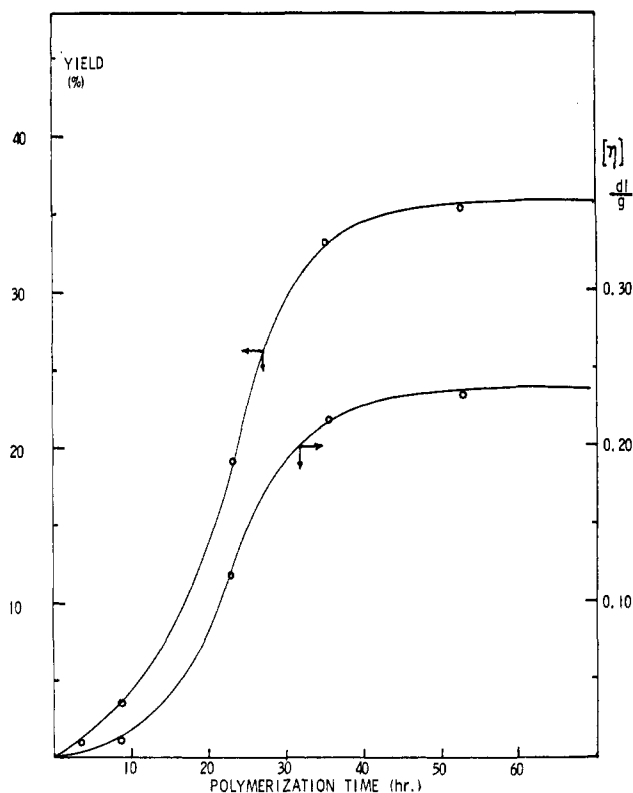
Figure 1. Time dependence of the yield (upper curve) of poly(α-phenylethyl isocyanide): 25°, c = 0.22 g/ml of heptane, air, concentrated H_2SO_4; and time dependence of polymer intrinsic viscosity (lower curve): 30°, toluene.

marked solvent dependence—proceeding much better in n-heptane than in pure monomer or chloroform. This experience is similar to Deyrup's, wherein polar media diminish the catalytic effect of acids.[123] On the other hand, a completely homogeneous system for the polymerization has recently been found, involving p-toluenesulfonic acid in dioxane,[109] and promises future kinetic studies.

Isocyanides polymerized by variations of this system include α- and β-phenylethyl, phenyl, o-tolyl, n- and cyclohexyl, n-, sec-, and tert-butyl, n- and isopropyl isocyanides, dl-methyl α-isocyanopropionate, methyl cyclopropylcarboxylate, and copolymers thereof.[1,105,109,124-126]

An unusual effect of structure has appeared. Droplets of concentrated sulfuric acid, dispersed in n-heptane, polymerize sec-butyl isocyanide (50–66% yields)[125] and isopropyl isocyanide (20–25% yields) at 30°[126] whereas only sparse amounts of polymers are isolated from the corresponding straight-chain alkyl isomers. (However, n-butyl isocyanide is polymerized by 12 M H_2SO_4 at −78° in 23% yield.[125]) At 30° n-propyl and n-butyl isocyanides yield complex product mixtures which show infrared absorptions at 1670 and 1720 cm⁻¹, also observed in the 2,3-bis(alkyl-imino)azetidines.[128] Similarly, dl-methyl α-isocyanopropionate is polymerized, whereas the β-phenyl derivative

thereof and methyl α-isocyanoacetate tend to yield oligomers.[109] Methyl α-isocyano-β-phenylpropionate, prepared in the basic medium of a tertiary amine, is usually contaminated with a similarly boiling substance having infrared absorption at 1510 and 1580 cm⁻¹, as is found in oxazoles. The formation of a 5-benzyl-4-methoxyoxazole is reasonable and is in analogy with ring closure proposed recently in acylations of α-metalated isocyanides.[126a]

Successful polymerizations require substantially pure monomer, and consequently, a monomer and a polymerizing system which are relatively free of conjunct reactions. Apparently, branching in alkyl isocyanides favor polymerization over conjunct reactions, in spite of the large negative entropy change which must accompany polymerization.[107,108] As pointed out above, tertiary alkyl isocyanides are prone to rearrangements under acid catalysis.[121]

2. Lewis Acid Catalysis

Typically these reactions are conducted at low temperatures (−80 to 0°) and are very fast. Since no truly soluble polyisocyanides have been synthesized by this method, the polymer molecule weights produced are unknown. An estimate of 1900–3700 was offered for the molecular weight of poly-(cyclohexyl isocyanide), assuming no transfer reactions in the $BF_3 \cdot O(C_2H_5)_2$-catalyzed polymerization.[41] The polymer is insoluble in all solvents tried but melts in the range 329–340°. This polymerization has become the basis of one patent.[8]

Boron trifluoride etherate has been used to polymerize the following isocyanides: ethyl, n- and sec-butyl,[127] cyclohexyl,[41] phenyl,[104,127] p-anisyl, p-chlorophenyl,[127] and p-tolyl.[127,128] Recently, binary copolymers of methylene (from diazomethane) with isocyanides,[128] and of cyclohexyl isocyanide with aryl isocyanides, have been prepared,[127] and a few copolymerization reactivity ratios have been calculated for the latter series. The attempted copolymerization of cyclohexyl isocyanide and trioxane with boron trifluoride etherate gave only mixtures of homopolymers.[41] Cyclohexyl isocyanide and acetaldehyde with the same catalyst gave cyclic oligomers and some low molecular weight, chloroform-soluble copolymer.[129]

The mixed salt, $NaAlCl_4$,[109] and $SnCl_4$[104] have also been used successfully as polymerization catalysts. Cyclohexyl isocyanide is not polymerized by $SnCl_2$ or $FeCl_3$. Ugi and Fetzer reported that 1% molar acetyl chloride oligomerized cyclohexyl isocyanide;[118] the same reagent, however, failed to yield solid products from n-propyl isocyanide.[109]

Klages and Mönkemeyer suggested that Friedel–Crafts catalysts do not function by binding the electron pair on the isocyanide carbon atom, for which adduct they would predict a good stability inconsistent with a polymerizing capability at low temperature.[45] They propose, instead, that polymerization occurs by way of trace amounts of a surely active energy-rich complex in which the catalyst is bonded to the nitrogen electron pair.

(125) F. Millich and G.-M. Wang, Abstracts, 6th Midwest Regional Meeting of the American Chemical Society, Lincoln, Nebr., Oct 29, 1970.

(126) S. Kapur, M.S. Thesis, University of Missouri-Kansas City, 1971.

(126a) U. Schöllkopf and R. Schröder, Angew. Chem, Int. Ed. Engl., 10, 333 (1971).

(127) Y. Yamamoto and N. Hagihara, Nippon Kagaku Zasshi, 89, 898 (1968).

(128) S. Iwatsuki, K. Ito, and Y. Yamashita, Kogyo Kagaku Zasshi, 70, 1822 (1967).

(129) T. Saegusa, N. Taka-ishi, and H. Fujii, Polymer Lett., 5, 779 (1967).

3. Decomposition of Metallo–Isocyanide Complexes

The reaction conditions for this polymerization route must depend on the instabilities of some metallo–isocyanide complexes. Stabilities of known isocyanide complexes range very widely (cf. section IIB). Inherently stable isocyanide complexes may be altered by chemical attack. Inherently unstable isocyanide complexes may be used without isolation, by in situ generation through ligand exchange between isocyanides and coordinated metals.

Yamamoto, et al., found that nickel and cobalt carbonyls polymerized cyclohexyl isocyanide in benzene during 5 hr of heating at 100°.[104] Under the same conditions the carbonyl compounds of Cr, Mn, and Mo failed, and Fe(CO)₅ gave only a 5% yield of polymer. Cyclopentadienyl derivatives of Ni and Co succeeded in the same procedure, whereas those of Fe and V failed.[104] Thus, active Co and Ni complexes which polymerize cyclohexyl isocyanide at 100° include $Co(CO)_8$, $Ni(CO)_4$, $(\pi\text{-}C_5H_5)_2Co$, $(\pi\text{-}C_5H_5)_2Ni$, $(\pi\text{-}C_5H_5)Co(CO)_2$, $[(\pi\text{-}C_5H_5)Ni(CO)]_2$, $Ni(CO)_3[(C_6H_5)_3P]$, and $Ni(CO)_2[(C_6H_5)_3P]_2$. The polymerization of tert-butyl isocyanide is reported to occur upon heating the monomer at 30–60° in the presence of a nickel complex formed by the alkylation of $Ni(tert\text{-}C_4H_9NC)_4$ with CH_3I.[87] A Japanese patent has been issued on the use of group VIII metal catalysts for the polymerization of isocyanides.[130]

4. Spontaneous Polymerizations and Polymerizations in the Presence of Ground Glass

Isocyanides have been reported from time to time to undergo spontaneous polymerization. The original sample of poly(α-phenyl isocyanide) occurred in this manner, and characterization showed it to be a high polymer.[1,105] At times the polymerizations have taken place during or shortly following distillation of the isocyanide. In most cases of reported spontaneous polymerizations one may assume that the polymerizing monomer contacted glass surfaces.

The rates of spontaneous polymerizations of isocyanides give the impression of very wide variation: at one extreme the isocyanide may be unperturbed for months to years; at the other extreme the same monomer can show an explosive rate. Lewis acid initiated polymerizations of isocyanides at very low temperatures are characterized by very rapid rates, but at room temperature these reactions, unlike many spontaneous isocyanide polymerization, are most often attended by colored byproducts and yield-limiting conjunct reactions, if not also prohibitively low product molecular weights. Most of the ground-glass joints and porous fritted ware observed to cause polymerization probably were made of sodium borosilicate glass. The surface of such a glass is covered with silanols, boronols, and Lewis acid sites, and is acidic in nature. Thus, these reactions may ultimately come to be classified with methods B.1 and B.2 above.

Such reactions may also have unique features.[107] The difficult steric requirement of compacting bulky substituents into the polymer constitutes a very unfavorable entropy change.[107,108] It is possible that polymerization is assisted

by an adsorptive surface through concentration, immobilization, and spacial ordering of the monomer as a preliminary act to bond formation. Polyisocyanides are all insoluble in their respective monomers, and few can be dissolved in solvents; thus, spontaneous polymerizations, once initiated, have almost always been heterophasic. Features like these may explain the great effectiveness in surface-promoted polymerization of isocyanides.

D. POLYMER PROPERTIES

The proposed structure of polyisocyanides (see below) are distinguished from those of condensation and ordinary vinyl polymers. The prevalent backbone substitution introduces severe conformational restrictions which are more pronounced than exist in vinyl polymers or polypeptides. Consequently, polyisocyanides promise to hold some new experiences in the exciting investigations of the molecular structure–physical properties relationships taking place today in polymer chemistry. The first characterization data of polyisocyanides seem to bear out the expectation and shall be reviewed here.

Prior to the first characterization of a polyisocyanide in 1965, the terms "polymer" and "resin" had been used indiscriminantly, and "polymer" had also been applied to substances which upon cryoscopic determination in benzene showed average degrees of polymerization, $\overline{DP}$, of 2–3.[96,97] It is now apparent that most known homopolymers (oligomers?) are not soluble without chemical alteration, poly(α- and β-phenylethyl isocyanide) and poly(dl-methyl α-isocyanopropionate) excepted.

The early reports of soluble "polymers" deserves reinvestigation. Also, many samples of poly(α-phenylethyl isocyanide) have been well characterized by osmometry, light scattering, viscometry, gel permeation chromatography, etc., to have $\overline{M}_w = 5 \times 10^4\text{-}2 \times 10^5$, and $\overline{M}_w/\overline{M}_n = 1.6\text{-}3.1$; nevertheless, it has been found that the high polymer depresses the freezing point of benzene to the degree, surprisingly, equivalent to apparent $\overline{DP} = 2\text{-}3$.[124] This is an unexplained anomaly and a challenging physical phenomenon.
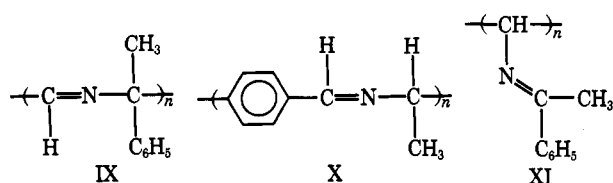
Polymerization of the optically active α-phenylethyl isocyanides ($[\alpha]^{27}D \pm 40$ deg cm²/g) yield polymers with values of very high molar specific rotation per mer (i.e., $M^{27}D > 500$ deg cm²/g in toluene).[108] This gives evidence of a coupling of transition dipoles of the absorbing chromophores and probably of an organized macromolecular structure. This and X-ray data indicate a tightly structured molecule.[107] Of the various conceivable structures, infrared spectral analysis is only consistent with the formula VI, or
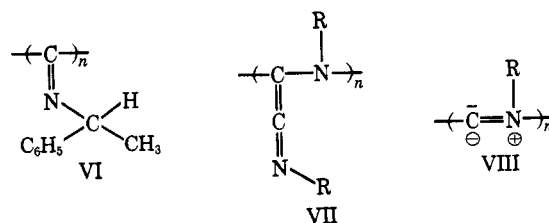
the less likely structure (possible by tautomeric, e.g., sigmatropic, rearrangement) XI.[107]

Structured as this polyisocyanide is, with bulky substitution on each backbone atom, the polymer should serve as a rare and important model substance for physico-chemical

(130) N. Hagihara, Y. Yamamoto, and S. Otsuka, Japanese Patent 69 01,233; Chem. Abstr., **70**, 97417 (1969).

$$\begin{array}{ccc}
\overset{\displaystyle CH_3}{\underset{\displaystyle H}{\underset{\displaystyle C_6H_5}{-(C=N-C-)_n}}} & \overset{\displaystyle H \quad H}{\underset{\displaystyle CH_3}{-\langle \bigcirc \rangle -C=N-C-)_n}} & \overset{\displaystyle -(CH-)_n}{\underset{\displaystyle C_6H_5}{\underset{}{N=C-CH_3}}} \\
IX & X & XI
\end{array}$$

investigations of bulk and solution properties. Derivatives of the polymer, such as the saturated polyamine, should likewise serve for such studies, and for investigations of adsorption, ion-exchange, chelation, and catalysis phenomena, with relevance to physical and chemical properties of biopolymers.

The recently synthesized alkyl and aryl polyisocyanides have been described above as insoluble in all solvents tried. However, di- and trichloroacetic acids (and sulfuric acid in some cases) succeed in "dispersing" many of the polyisocyanides. It is probable that these acids function by first protonating the polyisocyanides and then dispersing the resultant polycationic product, rather than functioning solely by purely thermodynamic mixing. For instance, poly-(o-tolyl isocyanide) powder changes from bright yellow to dark brown on contact, is dispersed in, and can be precipitated on addition of water as a dark brown, gelatinous substance from trichloroacetic acid solution; but with aqueous alkali it recovers its original appearance and is insoluble in all solvents and lesser acids.

Dispersion in the chloroacetic acids shows additional complications. The presence of some water produces an effective hydrolytic medium at room temperature.[131] Viscosities of polyisocyanide solutions in dichloroacetic acid are observed to decrease markedly in a 24-hr period.[104,126] Viscometry conducted in this medium cannot be interpreted without understanding of the solute hydrodynamic volume and the phenomenon of the viscosity time dependence.

A large dissociation constant is not a sufficient criterion for a potential dispersing agent of insoluble polyisocyanides, since some polyisocyanides which are dispersed by dichloroacetic acid are not dispersed by trifluoroacetic, hot trichloroacetic, or cold sulfuric acids.[104]

In concentrated sulfuric acid, aromatic polyisocyanides are subject to sulfonation. Poly(cyclohexyl isocyanide) was reported to be insoluble in 97% H_2SO_4.[8,41] In contrast, poly(isopropyl isocyanide) is "dissolved" in this medium and is reprecipitated by the addition of water. Infrared shows that structural change has taken place.[126] The difficultly soluble poly(sec-butyl isocyanide) is "dissolved" by the acidic hexafluoroisopropanol with some attendant browning of the solution.[109]

Distinctly different is the solubility of poly(α-phenylethyl isocyanide). It is soluble in more than 40 solvents, from which are calculated the values $\delta_d = 9.62$, $\delta_p = 2.18$, and $\delta_h = 2.52$ $(cal/cm^3)^{1/2}$ for the solubility parameters due to dispersion forces, permanent dipole–dipole forces, and hydrogen-bonding forces, respectively,[132] according to the Hansen treatment.[133] The square root of the sum of the squares of these values gives the more conventional cohesive energy density, having the value in this case $\delta = 9.56$

$(cal/cm^3)^{1/2}$. It is found that the value of δ_p may vary over a rather wide range for various good solvents for this polymer. In contrast, the solubility parameters of benzene, toluene, and xylene differ by only very small amounts, yet the decreasing solubility of this polyisocyanide in these solvents is easily discerned.

Low solubilities often correlate with high melting points. Both properties are in part associated with the limited gain in entropy possible for a restricted tightly wound conformation such as is probable for polyisocyanides. Poly(cyclohexyl isocyanide) is reported to melt above 329°,[41] but for most observed polyisocyanides the melting points appear to lie above or in the range of the polymer ceiling temperatures.

Thermogravimetric analyses of polyisocyanide homopolymers show sigmoidal initial weight losses of about 50% over wide temperature ranges, described in Table II. This pattern differs for poly(n-butyl isocyanide) in that the initial sigmodial curve reaches 90% weight loss. The poly(aryl isocyanide) shows the highest inflection point. Although the temperatures at which weight loss begins is difficult to estimate from the asymptotic curve, nearly all of the polyisocyanide samples apparently show losses which begin quite low and extend over a wide range of temperature. If further analysis establishes for one of these polymers that it is solely degrading to monomer, then the attainment of enthalpy and entropy differences for a monomer–polymer equilibration is feasible. However, previous study of poly-(α-phenylethyl isocyanide), prepared in the presence of air, revealed the incorporation of 0.5–1.8% oxygen[105] which is probably responsible for its initial random thermal chain cleavage at 110°.[108] The type of degradation of polyisocyanides, i.e., unzippering vs. random cleavage, in the temperature range of rapid weight loss has not yet been studied. The end groups of the homopolymers are unknown. Capping of polymer end groups can stabilize polymers against thermal degradation.

Debye–Scherrer diagrams have been reported for three polyisocyanides. Poly(α-phenylethyl isocyanide) and poly-(o-tolyl isocyanide) each show a sharp intense deflection at a value of $2\theta = 6.87°$, equivalent to a regular spacing of $d = 13.08$ Å.[107] The former polyisocyanide also shows a broad peak at $2\theta = 20.9°$ ($d = 4.36$ Å), and the latter at $2\theta = 14.0°$ ($d = 6.16$ Å) and 24.7° ($d = 3.65$ Å). Poly(cyclohexyl isocyanide) was not investigated at $2\theta = 6.87°$, but showed medium broad deflections at $2\theta = 15$ and 20°.[104] Attempts to grow crystals from poly(α-phenylethyl isocyanide) have not met with success.[109]

Generally, aryl polyisocyanides appear bright canary yellow, aliphatic are colorless to off-white, and aralkyl and polar substituted alkyl are pale yellow-brown. The tight helix conformation of bulky substituted polyisocyanides must prevent planar cis and trans geometries for vicinal imine groups, such as are assumed in conjugated α-diketones. The origin of color among the aralkyl polyisocyanides is intriguing. Weakly absorbing chromophores exist in poly-(α-phenylethyl isocyanide) throughout the near-ultraviolet and visible spectral regions.[108] Optically active poly(α-phenylethyl isocyanide) has such high molar rotation (i.e., $M^{27}°D \cong 500$ deg cm^2/g) as to indicate a molecular arrangement in which the transition dipoles of the absorbing chromophore are coupled.[108] The intensity of color, visible by reflection and by transmission, for fractionated samples of

(131) F. Millich and W. A. Sulzen, unpublished results.
(132) F. Millich and C. M. Hansen, unpublished results.
(133) C. M. Hansen, Ind. Eng. Chem., Prod. Res. Develop., 8, 2 (1969).

Table II[109]

Thermogravimetric Degradation of Polyisocyanide Samples, R—N=(C)$_n$<

| R | Preparative conditions[a] | | | | | $[\eta]^{30}$/solvent (dl/g) | TGA range[b] T (°C) |
	H_2SO_4	Atm	T (°C)	Time (hr)	Yield (%)		
(CH₃)₂CH[c]	Concd	N₂	30	72	25	2.10[d]/Cl₂CHCOOH	320 (188, 275)
n-C₄H₉	12 M	N₂	−78	75	23	...	326 (80, 208)
CH₃CH₂CH(CH)₃	12 M	N₂	25	168	37	4.52[d]/Cl₂CHCOOH	305 (50, 255)
C₆H₁₁	Concd	N₂	25	46	18	...	305 (84, 236)
CH₃CH(COOCH₃)	Concd	Air	28	43	44	0.86/ClCH₂CH₂Cl	248 (60, 192)
C₆H₅CH(CH₃)	Concd[e]	Air	40	43	24	0.94/C₆H₅CH₃	270 (119, 232)
C₆H₅CH₂CH₂	Concd	Air	25	112	48	1.18/C₆H₅CH₃	343 (91, 200)
o-CH₃C₆H₄	Concd[e,f]	Air	50	20	..	...	421 (145, 377)
o-CH₃C₆H₄	Spontaneous	Air	25	...	50	...	396 (308, 361)

[a] Except where noted, samples were prepared in heptane by the method of Millich and Wang.[125] [b] The temperature at the inflection point (ca. 30% wt loss) of initial sigmoidal weight loss curve is given and, in parentheses, the temperatures at which loss apparently first begins and loss has reached 5%, respectively. Heating rates = 10 deg/min in N₂ or Ar atmosphere. The thermobalances used were DuPont Model 950 and Perkin-Elmer Model TGS-1. [c] Reference 126. [d] The intrinsic viscosities of polyisocyanides in dichloroacetic acid are unstable and were extrapolated to zero time. [e] Dibenzoyl peroxide (0.015 g/ml of monomer) was incorporated. [f] Method of Millich and Sinclair.[105]

poly(α-phenylethyl isocyanide) appears to decrease as molecular weight increases.[134]

The most distinctive infrared spectral absorption of polyisocyanides is that of the imine group, >C=N—, which generally occurs in the 1645–1615-cm⁻¹ region (KBr pellets). Most of the polyisocyanides also show two or three prominent, sharp absorption bands in the 910–825-cm⁻¹ region, which may be associated with motions of the polymer backbone.

The proton nmr spectrum of poly(α-phenylethyl isocyanide), in tetrachloroethylene solution, shows broad resonance bands at 25°, which show little change at 128°.[108] This result is consistent with the model of a stiff, tightly wound helical molecule. Solid-state nmr shows a broad-line dispersion and a superimposed relatively narrow wave.[134] The latter disappears as the temperature is lowered below −35°, and is undoubtedly associated with the substituent methyl groups. The broad-line absorption band undergoes a small decrease in the second moment in the temperature range of −85°. This transition is probably associated with backbone C–C bond twisting that consequently affects the interactions of vicinal substituent phenyl groups.[134a]

The reduced specific viscosity for fractionated samples of poly(α-phenylethyl isocyanide) ($\bar{M}_n$ = 1.09–12.6 × 10⁴) shows strict linear concentration dependence for 19 fractions (c = 1–10 g/l. in toluene at 30°), resulting in the value for the Staudinger–Mark–Houwink equation:[135] $[\eta]^{30°}_{C_7H_8}$ = 1.9 × 10⁷·$\bar{M}_n^{1.36}$. The high value of the exponent of $\bar{M}_n$ indicates a very stiff molecule.[134] Further, applying Simha's equation[136]

for an ellipsoid of revolution to a cylindrical model of the polymer,[137] a value of 15 Å can be calculated for the diameter of the cylinder,[134] in excellent agreement with the value of 15.1 Å previously reported from X-ray scattering data.[107] On the basis of the contrasting solubility of this polymer with most poly(alkyl isocyanides), the latter might be expected to be rod-like and have even greater rigidity.

Another interesting result is obtained from the viscosity data. The average value of the Huggins constant[138] for eight of the nine fractions of $\bar{M}_n$ > 38,000 and for the unfractionated sample is k = 0.59 ± 0.07; surprisingly, the value of k abruptly changes to 1.24 ± 0.06 for nine of ten of the remaining fractions of $\bar{M}_n$ < 32,000. The cause of this interesting polymer solution behavior is being pursued presently.

The chemistry of isocyanide polymerization, the physics of the polymer properties, and morphological studies are just now emerging, and promise experiences meriting scientific attention.

(134) E. W. Hellmuth and S. Y. Huang, unpublished results.
(134a) H. G. Hecht, "Magnetic Resonance Spectroscopy," Wiley, New York, N. Y., 1967, p 90.
(135) R. Houwink, J. Prakt. Chem., 155, 241 (1940).
(136) R. Simha, J. Phys. Chem., 44, 25 (1940).
(137) P. Doty, J. H. Bradbury, and A. M. Holtzer, J. Amer. Chem. Soc., 78, 947 (1956).
(138) M. L. Huggins, ibid., 64, 2716 (1942).