Reaction of Isocyanides with Mercuric Chloride

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Isocyanides reacted with mercury(II) chloride in dry tetrahydrofuran upon heating to afford low molecular weight polymers and oligomers. Isocyanides without bulky groups underwent polymerization catalyzed by mercury(II) chloride. Various heterocyclic oligomers were obtained from the reaction of 2,6-xylyl isocyanide with mercury(II) chloride.

Isocyanides have been reported to polymerize by many kinds of catalysis,[1,2] (a) protonic acids catalysis, (b) certain Lewis acids catalysis, (c) group VIII metal catalysis and (d) ground glass catalysis. On the other hand, little has been known about the oligomerization of isocyanides in spite of its utility for the synthesis of heterocycles and oligomeric derivatives.

In the course of studying the reaction of isocyanides with mercury(II) compounds,[3-5] we found that isocyanides react with mercury(II) chloride to give labile isocyanide complexes, and to afford cyclic oligomers and low molecular weight polyisocyanides upon heating. Here we report the oligomerization and polymerization of isocyanides *via* isocyanide-mercury(II) chloride complexes.

Results and Discussion

Cyclo-oligomerization of 2,6-Xylyl Isocyanide (I). 2,6-Xylyl isocyanide reacted with mercury(II) chloride to give 2,6-xylyl isocyanide-mercury chloride complex (II) at room temperature.[3] When I and mercury(II) chloride in molar ratio of 4: 1 were heated in THF at reflux for 5 h, two heterocyclic tetramers (III and IV) and one pentamer (V) were isolated in 1, 4, and 1% yield based on I, respectively. The complex II was also obtained in good yield. The compound III was converted to IV easily by hydrolysis in aqueous THF solution or in silica gel column chromatography. Elemental analysis and mass spectrum of III indicate that compound III consists of four molecules of I, one chlorine and one hydrogen atom. IR spectrum of III shows absorptions at 3420 due to ν_{NH}, 1670, 1640, and 1625 cm^{-1} due to $\nu_{C=C}$ and $\nu_{C=N}$. NMR spectrum exhibited a singlet at δ 3.76 due to NH proton, four sharp singlets around δ 2.0 due to methyl protons and two broad singlets around δ 7.0 due to aromatic protons. Compound IV was found to have the composition of four molecules of I and one molecule of water on the basis of elemental analysis and mass spectrum. In the IR spectrum, IV shows absorptions at 3370 and 3296 due to two ν_{NH}. The NMR spectrum of IV shows characteristic singlets at δ 4.32 and 5.04 due to NH protons in addition to signals due to methyl protons and aromatic protons. UV absorption pattern is similar to that of pyrrolin-2-one derivatives.[6] From these data,

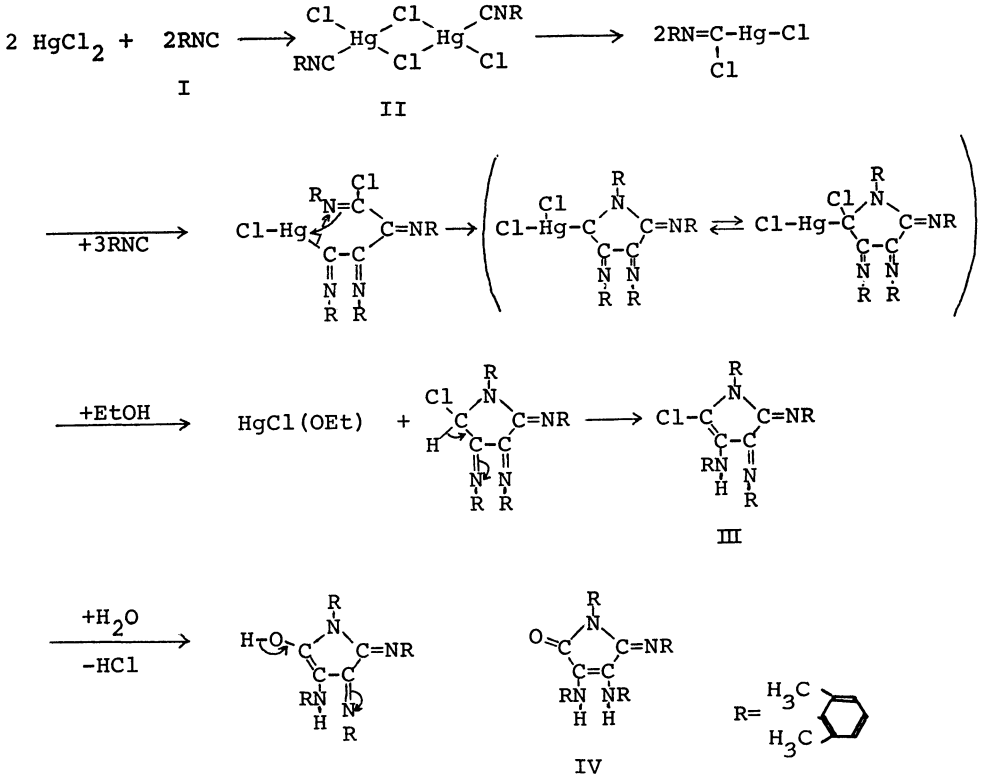

Fig. 1

III and IV were identified as 1-(2,6-xylyl)-2-chloro-3-(2,6-xylylamino)-4,5-bis(2,6-xylylimino)-2-pyrroline and 1-(2,6-xylyl)-3,4-bis(2,6-xylylamino)-5-(2,6-xylylimino)-3-pyrrolin-2-one, respectively. The formation of III and IV could be explained as following scheme. Insertion of I into Hg–Cl bond and successive insertion could form intermediate (A). Further insertion reaction presumably could hardly take place because of steric hindrance of I. Intramolecular addition of Hg–C bond to C=N forms complex (B), which converts to C. Subsequent proton shift of C could give III. The addition of ethanol to the reaction mixture enhanced the oligomerization. Thus, the oligomers III, IV, V, and blue crystalline hexamer (VI) were isolated in 4, 12, 3, and 0.2% yield, respectively. The reaction of phenylisocyanide–mercury(II) chloride complex with I gave small amounts of 1:1 co-oligomer (IV'), whose structure is similar to that of IV.

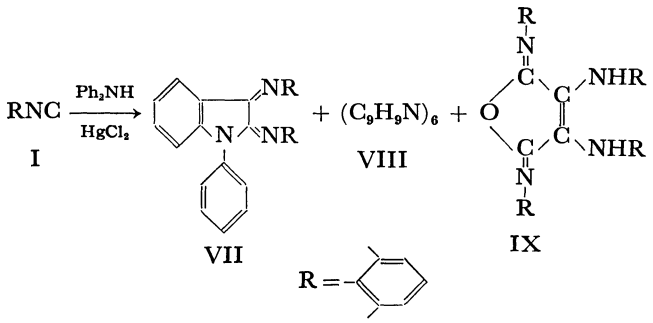

Fig. 2

Diphenylamine affected the oligomerization of I, though the role of diphenylamine is unclear. Heating a mixture of I, mercury(II) chloride and diphenylamine in THF solution gave red crystals (VII), brown crystalline hexamer (VIII) and orange yellow crystalline tetramer (IX) in 3, 21, and 31% yield, respectively. Elemental analysis and mass spectrum of VII indicate that VII is a 2:1 adduct of I and diphenylamine. IR and NMR spectra indicate that VII is an isatindiimine derivative. Compound IX was found to be an isomer of IV from elemental analysis and mass spectrum data. NMR spectrum exhibits that IX has a symmetrical molecular structure. Therefore, the compound IX was determined as 2,5-bis(xylylimino)-3,4-bis(xylylamino)furan. The compound I cannnot hold a polymer chain propagation and affords various heterocyclic oligomers.

Polymerization of Isocyanide. Isocyanides without bulky groups can polymerize in the presence of mercury(II) chloride. Heating a mixture of benzyl isocyanide and mercury(II) chloride in THF gave brownish powdery polymer In the similar manner, cyclohexyl and phenyl isocyanide gave brownish polymers. IR spectra of the polymers show absorptions at 1640—1650 and 3260—3370 cm^{-1} (weak) due to $\nu_{C=N}$ and ν_{NH}, respectively. Elemental analysis suggests that the polymers consist mainly of monomer unit and small amounts of water. The molecular weights of these polymers are 720—850. This indicates that the average degree of polymerization is seven to eight. These polymers are soluble in THF and chloroform, but insoluble

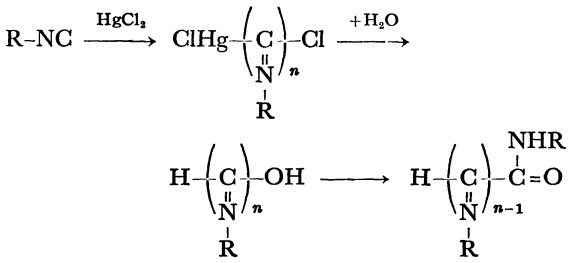

Fig. 3

in ether. The molecular weights of the polymers are far lower than that of polyisocyanides obtained by $BF_3 \cdot OEt_2$ or $SnCl_4$ catalysis.[2] High reaction temperature and high molar ratio of isocyanides to mercury(II) chloride are also responsible for the low molecular weight.

Experimental

The melting points are uncorrected. The IR spectra were recorded with a JASCO DS-402 spectrometer. The NMR spectra were measured with a JEOL TMN-TS-100 spectrometer. The mass spectra were taken with a JEOL SG-01 apparatus. Molecular weights of the polymers are measured with Hitachi-Perkin Elmer 115 Molecular Weight Apparatus using chloroform solution. Isocyanides were prepared by the method of Ugi and coworkers.[7]

Reaction of I with Mercury(II) Chloride: Mercury(II) chloride (0.68 g, 25 mmol) **I** (1.31 g, 10 mmol) and dry THF (10 ml) were mixed in a 30 ml conical flask under nitrogen and stirred for 5 h at reflux. The reaction mixture was filtered to remove white powder (Hg_2Cl_2, 18 mg). The filtrate was concentrated and treated with 20 ml of ether to remove II (0.89 g) by filtration. The filtrate was concentrated *in vacuo* and subjected to column chromatography on silica gel. The crystalline oligomers, III, IV, and V were isolated by using hexane–ether as an eluent. Recrystallization of III from hexane–ether gave purified reddish purple crystals, (53 mg, 3.8%), mp 195—197°. Found: C, 77.02; H, 6.79; N, 10.16 %. Calcd for $C_{36}H_{37}N_4Cl$: C, 77.05; H, 6.65; N, 9.98%. IR (KBr): 3420, 1670, 1645, 1625 cm^{-1}. NMR ($CDCl_3$): δ 1.99 (s, 6H), 2.02 (s, 6H), 2.12 (s, 6H), 2.36 (s, 6H), 3.76 (s, 1H), 6.70—6.90 (broad s, 9H), 7.12 (s, 3H). Mass spectrum: M^+= 561 (561).

Recrystallization of IV from hexane–dichloromethane gave purified orange yellow crystals, (14 mg, 1%), mp 201—203 °C. Found: C, 80.10; H, 7.33; N, 9.83%. Calcd for $C_{36}H_{38}ON_4$: C, 79.67; H, 7.06; N, 10.32%. IR (KBr): 3370, 3296, 1655, 1640 cm^{-1}. NMR ($CDCl_3$): δ 1.88 (s, 6H), 2.05 (s, 6H), 2.23 (s, 6H), 2.36 (s, 6H), 4.32 (s, 1H), 5.04 (s, 1H), 6.63 (s, 3H), 6.66 (s, 3H), 6.93 (s, 3H), 7.22 (s, 3H). UV $\lambda_{max}^{CH_2Cl_2}$: 263 (ε, 26×10^4), 452 nm (4.7×10^3). Mass spectrum: M^+=542 (542).

V was recrystallized from hexane–dichloromethane to give purple crystals, (13 mg, 1%) mp 159—161 °C. Found: C, 82.65; H, 7.14; N, 10.67%. Calcd for $C_{45}H_{45}N_5$: C, 82.40; H, 6.92; N, 10.68%. IR (KBr): 1666, 1612 cm^{-1}. NMR ($CDCl_3$): δ 1.36 (s, 9H), 1.67 (s, 3H), 1.93 (s, 6H), 2.09 (s, 3H), 2.18 (s, 3H), 2.27 (s, 3H), 2.44 (s, 3H), 5.2—5.6 (m, 2H), 6.0—6.15 (m, 1H), 6.60—6.90 (broad s, 9H), 7.05 (broad s, 3H). Mass spectrum: M^+=655 (655).

Reaction of I with Mercury(II) Chloride in the Presence of Ethanol: A mixture of I (2.62 g, 20 mmol), mercury(II) chlo-

Table 1. Polyisocyanide obtained from the reaction of isocyanide and mercury(II) chloride

Polyisocyanide	Yield (%)	Mp (°C)	MW	IR (cm^{-1})	Elemental analysis C%	H%	N%
Benzyl	67	90—93	850	1640, 1600, 3370 (W)	80.09 (80.30) [a]	5.90 (6.09) [a]	11.83 (11.70) [a]
Cyclohexyl	49	124—128	820	1650, 3260 (W)	73.80 (75.30) [b]	10.05 (10.11) [b]	12.40 (12.54) [b]
Phenyl	74	120—123	720	1638, 1600, 3360 (W)	78.68 (79.58) [c]	5.00 (5.00) [c]	13.27 (13.25) [c]

a) Calcd for $(C_6H_5CH_2NC)_7+H_2O$. b) Calcd for $(C_6H_{11}NC)_7+H_2O$. c) Calcd for $(C_6H_5NC)_7+H_2O$.

ride (1.36 g, 5 mmol), dry THF (20 ml) and ethanol (2 ml) was heated at reflux with stirring for 8 h under nitrogen. Hg_2Cl_2 (150 mg) and II (2.238 g) were removed by filtration. The oligomers, III (334 mg, 11.9%), IV (112 mg, 4.1%), V (81 mg, 3.1%) and VI (5 mg, 0.2%), were isolated from the reaction mixture with a chromatography on silica gel. The compound VI was recrystallized from hexane–dichloromethane to give purified blue crystalline hexamer, mp (decompose) 266—267 °C. Found: C, 81.83; H, 7.05; N, 10.50%. Calcd for $C_{54}H_{54}N_6$: C, 82.40; H, 6.92; N, 10.68%. IR (KBr): 1655, 1580, 1465 cm^{-1}. NMR ($CDCl_3$): δ 1.68 (s, 12H), 2.00 (s, 12H), 2.24 (s, 12H), 6.51 (s, 6H), 6.71 (broad s, 12H). Mass spectrum: $M^+=786$ (786).

Conversion of III to IV: The compound III (101 mg) was heated in aqueous THF at reflux for 0.5 h. The red color of the reaction mixture turned to orange yellow. The reaction mixture was dried over sodium carbonate, concentrated *in vacuo* and chromatographed on silica gel. The compound IV was isolated (92 mg, 94.5%).

The compound III was also completely hydrolyzed to IV, when keeping in silica gel column chromatography for 8 h.

Co-oligomerization of Phenyl Isocyanide with I. Phenyl isocyanide (0.42 g, 4 mmol) and mercury(II) chloride (550 mg, 2 mmol) were mixed in dry THF (10 ml) cooling with Dry Ice–methanol under nitrogen to prepare phenyl isocyanide–mercury(II) chloride complex.

I (1.053 g, 8 mmol) was added to the mixture. The reaction mixture was warmed to room temperature with stirring for 1 h, then heated at reflux for 4 h. The reaction mixture was concentrated *in vacuo*, treated with ether to remove polyphenyl isocyanide and II as precipitates. The filtrate was concentrated and subjected to column chromatography on silica gel to isolate orange yellow crystals (30 mg, 3.0%) and yellow crystals (8 mg). The orange yellow crystals were recrystallized from hexane–dichloromethane to give purified IV′, mp. 176—177 °C. Found: C, 78.76; H, 6.69; N, 11.28 %. Calcd for $C_{32}H_{30}ON_4$: C, 78.98; H, 6.21; N, 11.52%. IR (KBr): 3365, 3305, 1725, 1655, 1645, 1602 cm^{-1}. NMR ($CDCl_3$): δ 2.03 (s, 6H), 2.61 (s, 6H), 4.7 (broad s, 1H), 6.42 (broad s, 6H), 6.78 (s, 5H), 7.24 (s, 5H). Mass spectrum: $M^+=486$ (486).

Reaction of I with Mercury(II) Chloride in the Presence of Diphenylamine: Diphenylamine (0.85 g, 5 mmol) was added to the mixture of mercury(II) chloride (0.67 g, 2.5 mmol), I (1.31 g, 10 mmol) in dry THF (10 ml). The reaction mixture was heated at reflux for 5 h with stirring under nitrogen. The reaction mixture was concentrated and treated with 20 ml of ether to remove mercury(I) chloride, diphenylamine and II by filtration. The filtrate was concentrated and chromatographed on silica gel. Three compounds were isolated by using hexane–ether as an eluent. Recrystallization from hexane–ether gave the purified 2:1 adduct VII (36 mg, 3.3%), mp 178—180 °C. Found: C, 84.02; H, 6.50; N, 9.57%. Calcd for $C_{30}H_{27}N_3$: C, 83.88; H, 6.34; N, 9.78%. IR (KBr): 1672, 1637, 1589 cm^{-1}. NMR ($CDCl_3$): δ 1.91 (s, 6H), 2.11 (s, 6H), 2.11 (s, 6H), 6.4—6.85 (m, 5H), 6.93 (s, 3H), 7.20 (s, 3H), 7.25—7.60 (s, 4H). UV $\lambda_{max}^{CH_2Cl_2}$: 260 (ε, 4.1×10^4), 245 nm (2.85×10^3). Mass spectrum: $M^+=429$ (429).

Recrystallization of a brown compound from hexane–dichloromethane gave the purified VIII, (142 mg, 21.2%) mp. 295—298 °C. Found: C, 82.13; H, 7.06; N, 10.69%. Calcd for $C_{54}H_{54}N_6$: C, 82.40; H, 6.92; N, 10.68%. IR (KBr): 3380, 1671, 1625, 1507 cm^{-1}. NMR ($CDCl_3$): δ 1.84 (s, 6H), 2.15 (s, 6H), 2.24 (s, 6H), 3.98 (s, 1H), 6.59 (s, 3H), 6.73 (s, 3H), 6.83 (s, 3H). UV $\lambda_{max}^{CH_2Cl_2}$: 279 (ε, 49×10^5), 442 nm (5.8×10^5). Mass spectrum: $M^+=786$ (786).

Recrystallization of an orange compound from hexane–dichloromethane gave the purified IX, (213 mg, 30.7%), mp 211—212°. Found: C, 79.81; H, 6.62; N, 10.27%. Calcd for $C_{36}H_{38}ON_4$: C, 79.97; H, 7.06; N, 10.32%. IR (KBr): 3355, 1734, 1650, 1590 cm^{-1}. NMR ($CDCl_3$): δ 2.12—2.20 (broad m, 24H), 4.51 (s, 2H), 6.5—7.1 (broad m, 12H). UV $\lambda_{max}^{CH_2Cl_2}$: 276 (ε, 3.0×10^4), 487 nm (5.8×10^3). Mass spectrum: $M^+=542$ (542).

Polymerization of Isocyanides in the Presence of Mercury(II) Chloride. Benzyl isocyanide (1.20 g, 10 mmol) and mercury(II) chloride (0.672 g, 2.5 mmol) in 10 ml of dry THF was heated at reflux with stirring for 5 h under nitrogen. The reaction mixture was subjected to GLC analysis, and the formation of benzyl chloride (5% based on $HgCl_2$) was confirmed. White precipitates (Hg_2Cl_2, 280 mg) were removed from the reaction mixture by filtration. The filtrate was concentrated and 20 ml of ether was added to separate light brown powders, which were treated with $LiAlH_4$ in THF solution to remove mercury(II) by reduction. The brown powders were extracted with dichloromethane, dried over magnesium sulfate, concentrated and treated with ether–hexane to spectrate poly(benzyl isocyanide) as brown precipitates.

Poly(cyclohexy isocyanide) was obtained by the same procedure as that of poly(benzyl isocyanide).

The reaction of phenyl isocyanide (2.5 mmol, 20 mmol) with mercury(II) chloride (1.35 g, 5 mmol) was carried out at room temperature for 8 h and poly(phenyl isocyanide) was isolated by the similar manner as described in the reaction of benzyl isocyanide with mercury(II) chloride. Yield data, melting point, elemental analysis, IR data and molecular weight of these polymers are listed in Table 1.

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