The Synthesis and 1,4-Addition Type Ring-opening Polymerization of N-Substituted Cyclic Iminocarbonates

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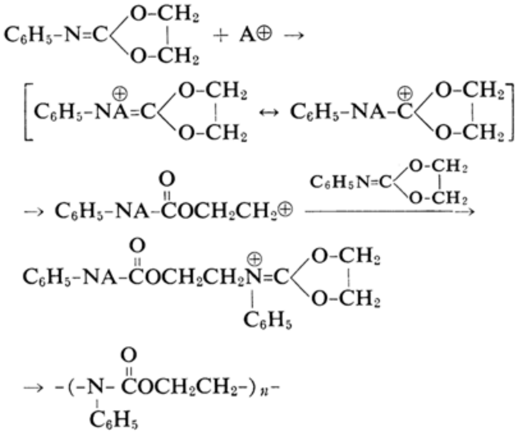
(Received December 11, 1963)

It has been shown in a previous paper that ethylene *N*-phenyl iminocabonate affords poly(ethylene *N*-phenylcarbamate) by ring-opening polymerization when treated with cationic catalysts.[1]

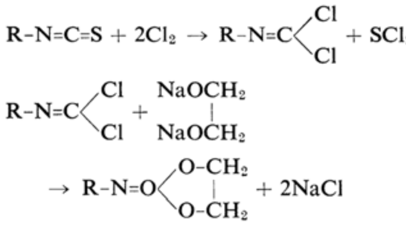


In the initiation step of the polymerization of ethylene *N*-phenyl iminocarbonate, a cationic catalyst adds to the imino group of the iminocarbonate to form a reactive addition compound. The addition compound in turn decomposes, with oxygen-carbon bond fission, to generate a new open-chained carbonium ion by the shift of an electron pair. The chain propagates by the rapid addition of the carbonium ion to a new monomer, a step which may be repeated many times.

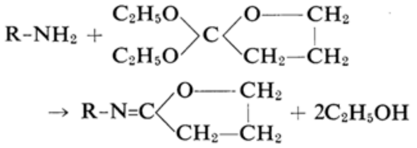
As is shown above, the polymerization proceeds by 1,4-addition; therefore, it can be termed a "1,4-addition type ring-opening polymerization." This involves the ring-opening polymerizations of such imino compounds as 2-iminotetrahydrofurans[2] and 2-imino-1,3-oxazolizines,[3] 4-methylene-1,3-dioxalane,[4] β-pinene,[5,6] diketene[7-9] and 1,4,6-trioxaspiro[4,4] nonane.[10]

In the present work, the syntheses of various *N*-substituted iminocarbonates and their ring-opening polymerization have been studied.

N-Alkyl and *N*-aryl ethylene iminocarbonates were prepared from the corresponding imidophosgenes and sodium ethylene glycolate according to a procedure similar to that used for ethylene *N*-phenyl iminocarbonate.[11] Alkyl and aryl imidophosgenes were prepared by passing chlorine into a chloroform or carbon tetrachloride solution of the corresponding alkyl and aryl isothiocyanates under cooling. The solvents, yields, physical properties and analysis for these imidophosgenes and iminocarbonates are listed in Tables I and II.



By a procedure similar to that used in the preparation of *N*-substituted iminotetrahydrofurans described in a previous paper,[2] the



preparation of *N*-substituted cyclic iminocarbonates from 2,2-diethoxy-1,3-dioxolane[12] and various primary amines was attempted. In contrast to the case of 2-iminotetrahydrofurans, the reaction of 2,2-diethoxy-1,3-di-

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[1] T. Mukaiyama, T. Fujisawa, H. Nohira and T. Hyugaji, *J. Org. Chem.*, **27**, 3337 (1962).

[2] T. Mukaiyama and K. Sato, This Bulletin, **36**, 99 (1963).

[3] H. Nohira, Y. Nishikawa and T. Mukaiyama, ibid., **37**, 797 (1964).

[4] M. Goodman and A. Abe, Am. Chem. Soc. Meeting, New York (1963), polymer preprints, Vol. 4, No. 2, p. 557.

[5] W. J. Roberts and A. R. Day, *J. Am. Chem. Soc.*, **72**, 1226 (1950).

[6] C. S. Marvel, J. R. Hanley, Jr., and D. T. Longone, *J. Polymer Sci.*, **40**, 551 (1959).

[7] J. Furukawa, T. Saegusa and N. Mise, *Makromol. Chem.*, **39**, 243 (1960).

[8] R. Oda, S. Munemiya and M. Okano, ibid., **43**, 149 (1961).

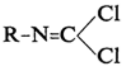
[9] J. Furukawa, T. Saegusa and N. Mise, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **65**, 254 (1962).

[10] K. Bodenbenner, *Ann.*, **623**, 183 (1959).

[11] T. Mukaiyama, T. Fujisawa and T. Hyugaji, This Bulletin, **35**, 687 (1962).

[12] This compound was prepared from ethylene carbonate, triethyl oxonium fluoroborate and sodium ethoxide by modified procedure for the preparation of carbon tetraethoxide by Meerwein et al., *Chem. Ber.*, **89**, 2060 (1956); yield 18%; b.p. 124~127°C. Found: C, 51.58; H, 8.86. Calcd. for $C_7H_{14}O_4$: C, 51.84; H, 8.70%.

TABLE I. THE SYNTHESIS OF ALKYL AND ARYL IMIDOPHOSGENES


$R{-}N{=}C\begin{smallmatrix}Cl\\Cl\end{smallmatrix}$

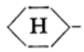
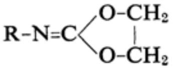
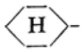
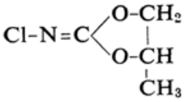
R	Solvent	Yield %	B. p. (m. p.) °C/mmHg		Analysis C, %	Analysis H, %	Analysis N, %
	CCl_4	95	100/30	Found	47.02	6.24	7.74
				Calcd.	47.02	6.16	7.77
n-C_6H_{13}-	CCl_4	52	94～96/24	Found	46.87	7.24	7.91
				Calcd.	46.17	7.20	7.69
p-Cl-C_6H_4-	CCl_4	71	80～82/1	Found	40.13	2.11	6.94
				Calcd.	40.24	1.91	6.71
p-NO_2-C_6H_4-	$CHCl_3$	68	120～130/8 (60～63)				

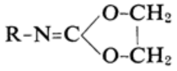
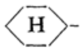
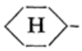
TABLE II. THE SYNTHESIS OF ETHYLENE N-SUBSTITUTED IMINOCARBONATES


$R{-}N{=}C\begin{smallmatrix}O{-}CH_2\\ \vert \\O{-}CH_2\end{smallmatrix}$

R	Yield %	M. p. (b. p.) °C (°C/mmHg)	Recrystallization solvent		Analysis C, %	Analysis H, %	Analysis N, %
	48	(110～113/0.3)		Found	62.56	9.02	8.09
				Calcd.	63.88	8.94	8.28
n-C_6H_{13}-	50	(94～96/0.18)		Found	62.70	9.94	8.05
				Calcd.	63.13	10.00	8.18
p-Cl-C_6H_4-	54	88～89	Ether	Found	54.67	4.05	7.09
				Calcd.	54.72	4.33	7.33
p-NO_2-C_6H_4-	15	121～123	Ether	Found	51.92	3.87	13.46
				Calcd.	51.11	3.65	14.38
Cl-	12	33～35	Ether	Found	29.47	3.14	11.76
				Calcd.	29.66	3.32	11.52
Br-	34	62～64*	Ether	Found	21.88	2.44	8.33
				Calcd.	21.71	2.42	8.43
	37	85～88/0.25		Found	35.76	4.74	9.94
				Calcd.	35.44	4.46	10.33

* Decomposition point.

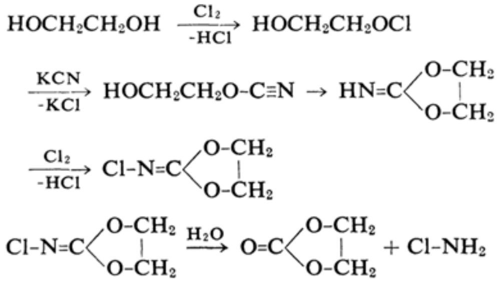
TABLE III. 1,4-ADDITION TYPE RING OPENING POLYMERIZATION OF ETHYLENE N-SUBSTITUTED IMINOCARBONATES

 R	Catalyst	Reaction Time hr.	Reaction Temp.	N-Substituted poly(ethylene carbamate) Yield %	M. p. (decomp. p.) °C	$[\eta]^{30°*}_{CHCl_3}$	Reprecipitation solvent
	$BF_3O(C_2H_5)_2$	96	Room	14	178～183	0.11	Chloroform-acetone
	H_2SO_4 (96%)	14	Room	32	185～190	0.20	Chloroform-acetone
n-C_6H_{13}-	$BF_3O(C_2H_5)_2$	70	Room	100	Oily	0.05	
p-Cl-C_6H_4-	$BF_3O(C_2H_5)_2$	Instant	100°C	56	135～142	0.24	Chloroform-petroleum ether
p-NO_2-C_6H_4-	$BF_3O(C_2H_5)_2$	27	Room	100	230～240	—	
Cl-	$BF_3O(C_2H_5)_2$	240	Room	98	(60)	0.14	Chloroform-petroleum ether

* $[\eta]^{30°}_{CHCl_3}$=intrinsic viscosity measured in chloroform at 30°C.

oxolane with primary amines, such as aniline and cyclohexylamine, did not give the corresponding iminocarbonates, even when they were heated at 130°C for 10 hr. in the presence of an acidic catalyst and most of the starting materials were recovered.

Next, *N*-halogeno cyclic iminocarbonates were prepared by the reactions of potassium cyanide, various glycohols and such halogenes, as chlorins and bromine in an alkaline solution. Their yields were comparatively low since they are rapidly hydrolyzed to yield ethylene carbonate when the reaction media become acidic.



$$\mathrm{HOCH_2CH_2OH}\xrightarrow[\mathrm{-HCl}]{\mathrm{Cl_2}}\mathrm{HOCH_2CH_2OCl}$$

$$\xrightarrow[\mathrm{-KCl}]{\mathrm{KCN}}\mathrm{HOCH_2CH_2O{-}C{\equiv}N}\rightarrow\mathrm{HN{=}C}\langle\begin{smallmatrix}\mathrm{O-CH_2}\\ |\\ \mathrm{O-CH_2}\end{smallmatrix}$$

$$\xrightarrow[\mathrm{-HCl}]{\mathrm{Cl_2}}\mathrm{Cl{-}N{=}C}\langle\begin{smallmatrix}\mathrm{O-CH_2}\\ |\\ \mathrm{O-CH_2}\end{smallmatrix}$$

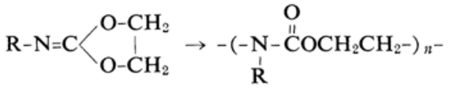
$$\mathrm{Cl{-}N{=}C}\langle\begin{smallmatrix}\mathrm{O-CH_2}\\ |\\ \mathrm{O-CH_2}\end{smallmatrix}\xrightarrow{\mathrm{H_2O}}\mathrm{O{=}C}\langle\begin{smallmatrix}\mathrm{O-CH_2}\\ |\\ \mathrm{O-CH_2}\end{smallmatrix}+\mathrm{Cl{-}NH_2}$$

It is to be noted that ethylene *N*-bromo iminocarbonate was unstable enough to decompose readily in the air and that it darkened within 8 hr., even when stored in an ethereal solution.

The *N*-halogeno cyclic iminocarbonates thus obtained were less reactive toward acidic substances than ethylene *N*-phenyl iminocarbonate,[11,13] and they did not react with benzoic acid when refluxed in benzene for 2 hr. and the starting materials were recovered quantitatively.

On the other hand, attempts to prepare unsaturated ethylene iminocarbonate by means of ester exchange between diethyl iminocarbonate and glycol, or by means of reductions of *N*-halogeno cyclic iminocarbonates with arsenious trioxide or with fluorene, failed.

When the ring-opening polymerization of *N*-substituted cyclic iminocarbonates was tried in the presence of such cationic catalysts as boron trifluoride etherate or sulfuric acid, the corresponding poly(ethylene *N*-substituted carbamates) were obtained, as Table III shows.



$$\mathrm{R{-}N{=}C}\langle\begin{smallmatrix}\mathrm{O-CH_2}\\ |\\ \mathrm{O-CH_2}\end{smallmatrix}\rightarrow-(-\underset{\mathrm{R}}{\underset{|}{\mathrm{N}}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OCH_2CH_2}-)_n-$$

Compared with ethylene *N*-phenyl iminocarbonate, the polymerization of these cyclic iminocarbonates, except for ethylene *N*-*p*-chlorophenyl iminocarbonate, took a long time and their intrinsic viscosities in chloroform were low.

Polyurethane obtained from ethylene *N*-chloro iminocarbonate was comparatively unstable and was gradually decomposed above 60°C, with the evolution of chlorine.

These results show that various poly(ethylene *N*-substituted carbamates) can be produced by the 1,4-addition-type ring-opening polymerization of cyclic iminocarbonates. On the other hand, the polyurethane can not be successfully produced from oxazolidone, 5-membered cyclic urethane, since it yields exclusively polyethyleneimine, with the evolution of carbon dioxide.

The ease of the 1,4-addition type ring-opening polymerization of these cyclic iminocarbonates may be interpreted in the following way: since the cyclic iminocarbonates are an enol isomer of cyclic urethane, which seems to be more unstable than the corresponding keto-form structure, it is reasonable to consider that these compounds are readily converted into the polymers with a keto-form structure by the ring-opening polymerization.

Experimental

Alkyl and Aryl Isothiocyanates. — Cyclohexyl isothiocyanate was prepared from cyclohexyl amine, carbon disulfide and mercuric chloride following the procedure of Skita.[14] *n*-Hexyl isothiocyanate was prepared from *n*-hexyl amine, carbon disulfide and ethyl chlorocarbonate by a method analogous to that used for the preparation of methyl isothiocyanate by Moore;[15] yield, 46%, b. p. 80~82°C/3 mmHg. *p*-Chlorophenyl and *p*-nitrophenyl isothiocyanates were prepared from corresponing anilines and thiophosgene according to the methods of Dyson[16] and Dyer.[17]

The Preparation of Cyclohexyl Imidophosgene. —A solution of 40 g. of cyclohexyl isothiocyanate in an equal volume of carbon tetrachloride was saturated with dry chlorine until the reaction mixture became dark red. Since an evolution of heat was noticed during the reaction, the reaction mixture was cooled in ice-water. After the solvent and sulfur dichloride had been removed by distillation, cyclohexyl imidophosgene was fractionated; yield, 48.0 g. (95%); b. p. 100°C/30 mmHg.

In a similar way, *n*-hexyl, *p*-chlorophenyl and *p*-nitrophenyl imidophosgenes were prepared from the corresponding isothiocyanates and chlorine as is shown in Table I.

The Preparation of Ethylene *N*-Cyclohexyl Iminocarbonate.—Into 5.4 g. (0.05 mol.) of sodium ethylene glycolate suspended in 30 ml. of dry benzene was added dropwise a solution of 9.0 g. (0.05 mol.) of cyclohexyl imidophosgene in 20 ml. of dry benzene with vigorous stirring. Then the

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[13] T. Mukaiyama, Y. Tamura and T. Fujisawa, This Bulletin, 37, 628 (1964).

[14] A. Skita and H. Rolfes, *Ber.*, **53**, 1242 (1920).

[15] M. L. Moore and F. S. Crossley, "Organic Syntheses," Coll. Vol. 3, 599 (1955).

[16] G. M. Dyson, ibid., Coll. Vol. 1, 165 (1948).

[17] E. Dyer and T. B. Johnson, *J. Am. Chem. Soc.*, **54**, 777 (1932).

reaction mixture was refluxed on a water bath for 2 hr. while being continuously stirred. It was then poured into water and extracted with benzene. After washing with water, the benzene solution was dried with calcium chloride. The benzene was then removed completely in vacuo and ethylene *N*-cyclohexyl iminocarbonate was distilled; yield, 4.0 g. (48%); b. p. 110～113°C/0.3 mmHg. The infrared absorption bands are 1700(s), 1410(ms), 1370(ms), 1250～1100(ms) broad, 1030(s) and 760(ms) cm^{-1}.

In a similar manner, ethylene *N*-*n*-hexyl, *N*-*p*-chlorophenyl and *N*-*p*-nitrophenyl iminocarbonates were prepared from the corresponding imidophosgenes and sodium ethylene glycolate as listed in Table II.

The Preparation of Ethylene *N*-Chloro Iminocarbonate.[18]—Into a solution of 16.0 g. (0.4 mol.) of sodium hydroxide, 13.0 g. (0.2 mol.) of potassium cyanide and 12.4 g. (0.2 mol.) of ethylene glycol in 80 ml. of water, was passed chlorine with vigorous stirring under cooling by ice-water until red litmus paper no longer changed to blue. When the aqueous solution, became neutral, ethylene *N*-chloro iminocarbonate floated on the surface of the solution. The iminocarbonate was filtered and was recrystallized from ether; yield, 2.9 g. (12%); m. p. 33～35°C. The infrared absorption bands are at 1650(s), 1400(ms), 1230(s), 1060(s) and 700(ms) cm^{-1}.

Similarly, propylene *N*-chloro iminocarbonate was prepared following the above method by using propylene glycol in place of ethylene glycol. Ethylene *N*-bromo iminocarbonate was also prepared by using bromine, of which about 50 g. was required, instead of chlorine as in the above experiment. The yields, physical properties and analysis for these iminocarbonates are also indicated in Table II.

The Polymerization of Ethylene *N*-Cyclohexyl Iminocarbonate.—Into 1.0 g. of ethylene *N*-cyclohexyl iminocarbonate was added a catalytic amount of boron trifluoride etherate; the mixture was then allowed to stand at room temperature for 14 hr. Then poly(ethylene *N*-cyclohexylcarbamate) was reprecipitated from chloroform-acetone. Yield, 0.14 g. (14%); m. p. 178～183°C. Its infrared absorption bands are at 1680(s), 1420(ms), 1230(ms), 1150(ms) and 760(ms) cm^{-1}.

Found: C, 63.23; H, 9.06; N, 7.96. Calcd. for $(C_9H_{15}O_2N)_n$: C, 63.88; H, 8.94; N, 8.28%.

The polymerizations of other *N*-substituted cyclic iminocarbonates were carried out in a similar method under the reaction conditions indicated in Table III in the presence of a small amounts of catalyst (7～10 mg.). The catalysts, yields, physical properties, intrinsic viscosities and solvents of reprecipitation for the polyurethane obtained are also shown in the same table.

Summary

As one of a series of studies of 1, 4-addition type ring-opening polymerizations, the synthesis and ring-opening polymerization of *N*-substituted cyclic iminocarbonates have been studied.

N-Alkyl and *N*-aryl cyclic iminocarbonates have been prepared by the reaction of sodium ethylene glycorate with the corresponding imidophosgenes. *N*-Halogeno cyclic iminocarbonates have been prepared from glycols, potassium cyanide and halogenes.

The ring-opening polymerization of the *N*-substituted cyclic iminocarbonates, which are considered to be cyclic enol derivatives of urethanes, in the presence of cationic catalysts gives the corresponding poly(ethylene *N*-substituted carbamates).

The authors wish to express their hearty thanks to Miss Toshiko Aoyagi for her microanalyses.

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[18] The preparation of this compound has aleady been published; H. E. Simnous, U. S. Pat. 2972620; *Chem. Abstr.*, 55, 14481 (1961).