this manner, as after one recrystallization, the 5-isomer is essentially eliminated. The formation of as much as 85% of the 8-nitro compound compares favorably with the 50% yield of 8-nitro derivative obtained on nitration of β-naphthylphthalimide.[5,6] The removal of the phthalimide group is so difficult that the method was abandoned by Ward and Wells[6] as a preparative process for 5- or 8-nitro-2-naphthylamines. On the other hand, the nitro Tobias acids can be desulfonated easily to form these nitroamines. The production of the 8-nitro-2-naphthylamine in this way avoids the use of the carcinogenic β-naphthylamine by substitution of the presumably innocuous Tobias acid. It also provides a starting material for an alternative route to 1,7-dinitronaphthalene and to the 1,7-diamine.

The preponderance of 8-nitration may be ascribed to the peri influence of the 1-sulfonic group as naphthalene-1-sulfonic acid has long been known to nitrate in the 8 (peri) position, this being the first step in the commercial process for 8-aminonaphthalene-1-sulfonic acid (peri acid).

Prior acetylation of the amine group in Tobias acid did not change greatly the isomer distribution in the product, and no 6-nitration was observed as is the case with 2-acetylaminonaphthalene.[6,7]

The mixture of nitro Tobias acids could not be separated because of close similarity in properties. It was therefore analyzed directly.

Dinitration of Tobias acid was not successful and no identifiable product was isolated on attempted nitration of 2-aminonaphthalene-1,5-disulfonic acid (sulfonated Tobias acid).

Experimental

Nitration at 0° or above resulted in desulfonation and formation of brown amorphous material. Temperature control was therefore important and a Dry Ice–alcohol bath was used.

Nitro Tobias Acids.—Concentrated sulfuric acid (96%, 120 ml.) was cooled to −5 to −10° and treated slowly with 11.15 g. (0.05 mole) of Tobias acid with stirring. Most was soluble and the liquid was cooled further to −15° and addition of dry powdered potassium nitrate was started. A 6-g. sample (0.059 mole) of this was added in 20 min. while keeping the temperature between −10 and −16°. The brown solution was stirred 40 min. in this temperature range and then poured onto 0.5 kg. of ice. The precipitated product was filtered off and washed, and then extracted with cold dilute sodium carbonate solution. The filtered extracts were cooled to 5° and acidified with hydrochloric acid. After 3 hr. on ice, the tan crystalline powder was filtered off, washed with ice water, and dried. Two runs gave yields of 12.65 g. (94.4%) and 12.85 g. (95.9%). This product did not change on boiling its solution in sodium carbonate, but decomposed partly on storage for several months at room temperature. It was vacuum dried for analysis.

Anal. Calcd. for $C_{10}H_8SO_5$: S, 11.94. Found, S, 11.96.

Desulfonation of Nitro Tobias Acids.—A mixture of 5 g. (18.65 mmoles) of the nitrated Tobias acid and 70 ml. of 45% sulfuric acid was refluxed 40 min. It was diluted while hot to 1 l. and made alkaline with sodium hydroxide solution. The suspension was cooled to 10° for 1.5 hr., and the precipitated material filtered, washed with water, and dried; yield, 3.10 g. or 88%. The yield is poorer with nitro Tobias acid which has been stored for some time. When recrystallized once from aqueous methanol, almost all of the 5-isomer was eliminated. The 8-nitro-2-naphthylamine thus obtained, was recrystallized from aqueous methanol and from benzene–hexane, and had m.p. 104–105.5°. An intimate mixture with material obtained by the procedure of Saunders and Hamilton[7] had m.p. 104–106°. Hodgson and Ratcliffe[8] give 104.5–105°. The infrared spectrum was identical with that of authentic material.[7]

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[5] H. H. Hodgson and J. H. Crook, *J. Chem. Soc.*, 1844 (1936).

[6] E. R. Ward and P. R. Wells, *ibid.*, 4859 (1961).

[7] C. R. Saunders and C. S. Hamilton, *J. Am. Chem. Soc.*, **54**, 636 (1932).

[8] H. H. Hodgson and J. Ratcliffe, *J. Chem. Soc.*, 1040 (1949).

A New Type of Ring-Opening Polymerization

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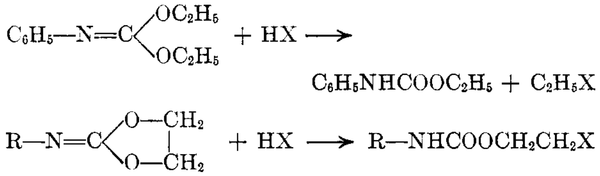
The reactions of diethyl N-phenyliminocarbonate and cyclic iminocarbonates with acids, such as hydrogen chloride, carboxylic acids, and phosphoric acid, have recently been reported to afford ethyl *N*-phenylcarbamate and the corresponding esters, and compounds containing urethane and ester linkages, respectively, as shown in the following equations.[1]

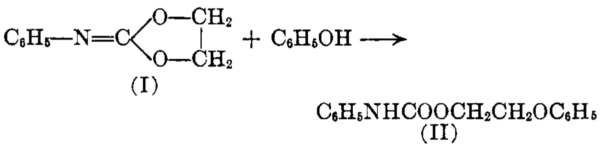


$$C_6H_5{-}N{=}C(OC_2H_5)_2 + HX \longrightarrow C_6H_5NHCOOC_2H_5 + C_2H_5X$$

$$R{-}N{=}C\begin{matrix}O{-}CH_2\\ |\\ O{-}CH_2\end{matrix} + HX \longrightarrow R{-}NHCOOCH_2CH_2X$$

Furthermore, it was found that cyclic iminocarbonates, such as ethylene N-phenyliminocarbonate and N,N′-*p*-phenylene bis(ethyleneiminocarbonate), react with phenols which are weaker acids than the acids mentioned above.

When ethylene N-phenyliminocarbonate (I) was refluxed with *p*-nitrophenol or phenol in dry benzene, β-*p*-nitrophenoxyethyl or β-phenoxyethyl N-phenylcarbamate was obtained in 53% and 55% yields, respectively.



$$\underset{(I)}{C_6H_5{-}N{=}C\begin{matrix}O{-}CH_2\\ |\\ O{-}CH_2\end{matrix}} + C_6H_5OH \longrightarrow \underset{(II)}{C_6H_5NHCOOCH_2CH_2OC_6H_5}$$

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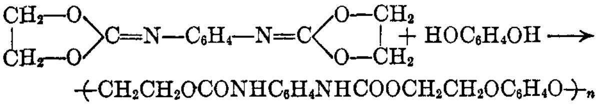
[1] T. Mukaiyama, T. Fujisawa, and T. Hyugaji, *Bull. Chem. Soc. Japan*, **35**, 687 (1962).

Similarly, N,N′-*p*-phenylene bis(ethyleneiminocarbonate) (II) reacted with hydroquinone in diethylformamide to produce polymer having alternating urethane and ether linkages.



$-\!(CH_2CH_2OCONHC_6H_4NHCOOCH_2CH_2OC_6H_4O)\!-_n$

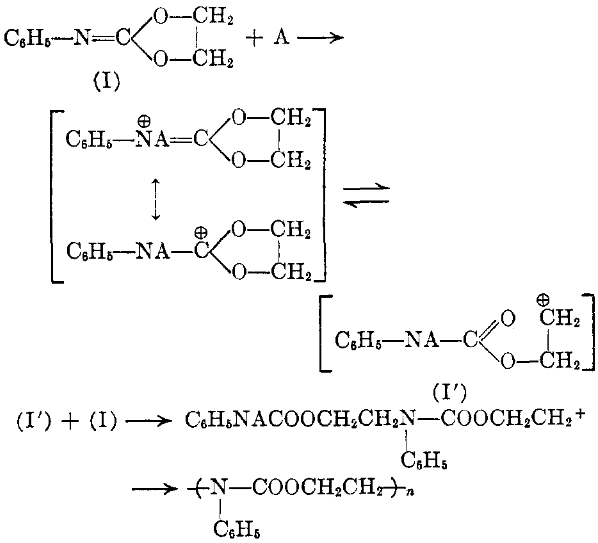
(II)

On the other hand, when a trace amount of boron trifluoride was added to a solution of ethylene N-phenyliminocarbonate in benzene, heat liberation was observed. From this solution a white solid separated gradually and it was reprecipitated from chloroform–acetone. This solid was confirmed to be poly(ethylene N-phenylcarbamate) (I_p) by means of infrared absorption spectrum which has characteristic bands attributable to urethane linkage (1720 cm.$^{-1}$) and to monosubstituted benzene ring (1600, 760, and 695 cm.$^{-1}$).

This is a ring-opening type polymerization, which presumably proceeds by a cationic chain mechanism through initial formation of the intermediate (I′) formed by the action of boron trifluoride.

Next, when a trace amount of boron trifluoride was added to a molten iminocarbonate melted at a temperature of 100°, the polymerization took place instantly and gave the same polyurethane (Ip).

The polymerization was likewise successfully carried out in the absence of catalyst, when it was kept in the molten condition at 100° for nineteen hours.



(I)

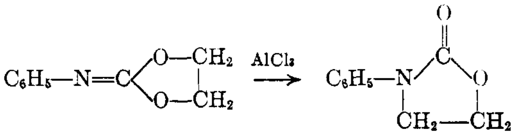
(I′)

$(I') + (I) \longrightarrow C_6H_5NACOOCH_2CH_2\underset{C_6H_5}{N}-COOCH_2CH_2^+ \longrightarrow -\!(\underset{C_6H_5}{N}-COOCH_2CH_2)\!-_n$

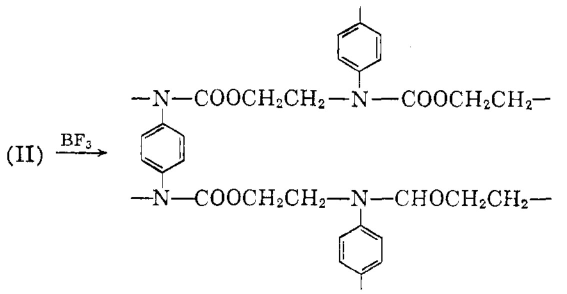
(Ip)

Further, the polymerizations of the iminocarbonate initiated by the following catalysts—such as titanium tetrachloride, stannic chloride, zinc chloride, ferric chloride, aluminum chloride, phosphoric acid, sulfuric acid (96%), or phosphorus pentoxide—were tried by the methods of bulk and solution polymerizations. These conditions of reaction and the characterization of the polyurethane produced in accordance with them are shown in Tables I and II.

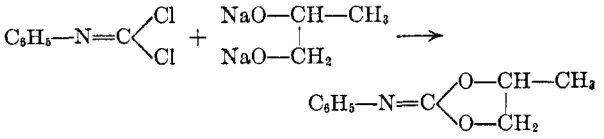
When aluminum chloride was used as a catalyst, the yield of the polyurethane was very low as shown in Table I. In this case, 3-phenyloxazolidone-2, a compound caused by the intramolecular rearrangement of the iminocarbonate, was obtained in a 60% yield instead of the polymer. This type of rearrangement was also carried out by the action of lithium chloride at 200°.[2]



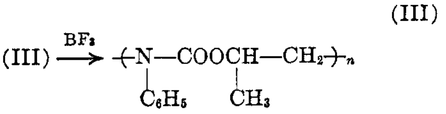
In a similar fashion, ring opening polymerization of N,N′-*p*-phenylene bis(ethyleneiminocarbonate) (II) was tried in the presence of a trace amount of boron trifluoride in a solution of dimethylformamide. After the solution was kept standing at room temperature for about twenty hours, dimethylformamide was removed and residue was washed with ether. The cross-linked polyurethane (IIp), which neither melted nor dissolved in any solvents and decomposed at 270°, was obtained.



1,2-Propylene N-phenyliminocarbonate (III), which was prepared from phenyl imidophosgene and sodium 1,2-propylene glycolate, also polymerized by ring opening in the presence of boron trifluoride at room temperature to produce poly(1,2-propylene N-phenylcarbamate) (IIIp) in high yield.



(III)



$(III) \xrightarrow{BF_3} -\!(\underset{C_6H_5}{N}-COO\underset{CH_3}{CH}-CH_2)\!-_n$

(IIIp)

Since the product obtained from the reaction of 1,2-propylene N-phenyliminocarbonate (III) with hydrogen bromide was identical with β-bromo-α-

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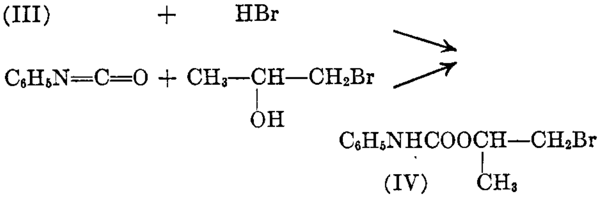
[2] K. Gulbins and K. Hamann, *Angew. Chem.*, **73**, 434 (1961).

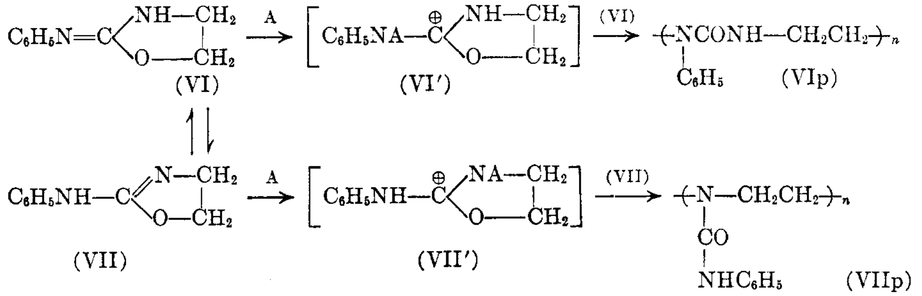
methylethyl N-phenylcarbamate (IV), which was prepared by another method from phenyl isocyanate and 1-bromopropanol-2, the polymerization seems to proceed by the bond fission between oxygen and methylene group to give poly(1,2-propylene N-phenylcarbamate) (IIIp).



$$(\mathrm{III}) + \mathrm{HBr} \qquad \mathrm{C_6H_5N{=}C{=}O} + \mathrm{CH_3{-}CH(OH){-}CH_2Br} \longrightarrow \mathrm{C_6H_5NHCOOCH(CH_3){-}CH_2Br}\ (\mathrm{IV})$$

larger part in polymerization under such a condition as bulk polymerization. These two compounds give different polymers, poly(ethylene-N-phenylurea) (VIp) and polyethyleneimine type polymer (VIIp). The polymers obtained were considered to be complex, because they are made up of by means of both type of polymerizations.

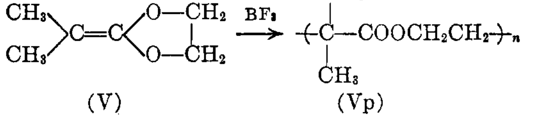
The reactivity of this pseudourea is quite small and melting point and viscosity of resulting polymer are low. This fact is attributed to the relatively larger stability of the cationic intermediate (VI′) and (VII′) compared with these of cyclic iminocarbonates and cyclic ketene acetals.



This type of polymerization was next extended to compounds which possess the structural possibility of ring opening polymerization, such as cyclic ketene acetals and iminooxazolidines.

Concerning the polymers of cyclic ketene acetals, McElvain[3] discussed their structure merely from analogy of the polymers of noncyclic ketene acetals and concluded their structure to be of the polyacetal type.

When the polymer obtained from the polymerization of dimethylketene ethylene acetal [V] in the presence of boron trifluoride was examined by infrared spectrum, strong enough absorption bands attributable to ester linkage (1735 cm.$^{-1}$ and 1250–1100 cm.$^{-1}$) were observed. This led to the conclusion that the polymer was mainly made up of ester linkage as expected.



(V) (Vp)

It was also established that 2-phenyliminooxazolidine (VI) was polymerized in the presence of cationic catalyst to give polymers having urea linkage (Table III). Since there are two tautomeric forms, 2-iminooxazolidine (VI) and 2-amino-2-oxazoline (VII), concerning this cyclic pseudourea,[4] it is difficult to say which of two forms take

Experimental

Reaction of Ethylene N-Phenyliminocarbonate (I) with *p*-Nitrophenol.—A solution of 0.8 g. of I and 0.7 g. of *p*-nitrophenol in 20 ml. of dry benzene was refluxed with stirring for 2 hr. After removal of benzene, β-*p*-nitrophoxyethyl N-phenylcarbamate was obtained and recrystallized from acetone; yield 0.8 g. (53%), m.p. 139–140°.

Anal. Calcd. for $C_{15}H_{14}N_2O_5$: C, 59.60; H, 4.67; N, 9.27. Found: C, 59.30; H, 5.05; N, 8.97.

Similarly, β-phenoxyethyl N-phenylcarbamate was obtained from the reaction of I with phenol and recrystallized from benzene; yield 55%, m.p. 74–75°.

Anal. Calcd. for $C_{15}H_{15}NO_3$: C, 70.02; H, 5.88; N, 5.44. Found: C, 70.41; H, 5.78; N, 5.39.

Reaction of N,N′-*p*-Phenylene Bis(ethyleneiminocarbonate (II) with Hydroquinone.—A mixture of 2.48 g. of II and 1.10 g. of hydroquinone in 10 ml. of dry dimethylformamide was heated on an oil bath at 100–110° with stirring for 2 hr., and then the mixture was poured into water with vigorous stirring to precipitate a polymer, alternating poly-(urethane–ether). The polymer was filtered off and washed several times with water and dried in vacuum; yield 3.02 g. (85%), m.p. 70°, d.p. 100°, $[\eta]^{30°}_{\mathrm{DMF}}$ 0.07.

Bulk Polymerization of Ethylene N-Phenyl Iminocarbonate (I).—One gram each of I was melted at about 100° on an oil bath, and to this molten iminocarbonate was added a small amount of catalyst (0.01–0.07% based on I). When the iminocarbonate solidified, the solid was dissolved in chloroform. After the solution was filtered, it was poured into an excess acetone to precipitate poly(ethylene N-phenylcarbamate) (Ip). Yields, melting points, and intrinsic viscosities were shown in Table I.

Anal. Calcd. for $(C_9H_9NO_2)_n$: C, 66.24; H, 5.56; N, 8.58. Found: C, 64.12; H, 5.47; N, 8.09.

When aluminum chloride was used as a catalyst, the molten iminocarbonate did not solidify after 24 hr., and the yield of polymer was low. In this case, 3-phenyloxazolidone-2 was obtained after removal of the solvent from the residual solution of the reprecipitation. It was recrystallized from ethanol; yield 0.6 g. (60%) m.p. 119–120°.

Solution Polymerization of I.—To a solution of 1.0 g. of I in 5 ml. of dry benzene was added the above mentioned

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[3] S. M. McElvain, *Chem. Rev.*, **45**, 487 (1949).

[4] E. Fromm, *et al.*, *Ann*, **467**, 240 (1928); R. H. Wiley and L. L. Bennett, Jr., *Chem. Rev.*, **44**, 467 (1949).

TABLE I

BULK POLYMERIZATIONS OF ETHYLENE N-PHENYLIMINOCARBONATE (I) AT 100°

Catalyst	Reaction time, hr.	Poly(ethylene N-phenylcarbamate)(Ip) Yield (%)	M.P.	$[\eta]^{30°}_{\mathrm{CHCl_3}}$[a]
Boron trifluoride	Instant	70	175–180°	0.88
Sulfuric acid (96%)	Instant	67	180–185	1.26
Titanium tetrachloride	3	57	186–188	0.82
Phosphorus pentoxide	13	49	200–237	3.85
Ferric chloride	14	51	178	0.26
Phosphoric acid	14	52	182	.75
Stannic chloride	16	55	178	.41
Zinc chloride	16	77	175–177	.29
Aluminum chloride	24	8	175–178	
No catalyst	19	46	176–179	.59

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

TABLE II

SOLUTION POLYMERIZATIONS OF ETHYLENE N-PHENYLIMINOCARBONATE (I) IN BENZENE

Catalyst	Reaction Time, hr.	Reaction Temp.	Poly(ethylene N-phenylcarbamate)(Ip) Yield, %	M.p.	$[\eta]^{30°}_{\mathrm{CHCl_3}}$
Boron trifluoride	1	Room	90	171–173°	0.33
Boron trifluoride	12	Reflux	88	175–182	.33
Titanium tetrachloride	12	Reflux	93	185–187	.96
Sulfuric acid (96%)	12	Reflux	97	177–180	.39
Phosphorus pentoxide	12	Reflux	90	177–182	.22

quantity of catalyst. After the reaction time as shown in Table II was over, benzene was removed and the residue was dissolved in chloroform. By the same procedure as mentioned above, poly(ethylene N-phenylcarbamate) (Ip) was obtained. Yields, melting points, and intrinsic viscosities were shown in Table II.

Anal. Calcd. for $(C_9H_9NO_2)_n$: C, 66.24; H, 5.56; N, 8.58. Found: C, 64.28; H, 5.57; N, 8.02.

Polymerization of N,N′-*p*-Phenylene Bis(ethyleneiminocarbonate) (II).—To a solution of 1.0 g. of II in 10 ml. of dry dimethylformamide was added a catalytic amount of boron trifluoride. After standing overnight, dimethylformamide was removed and residue was washed with acetone. The resulting polymer was cross-linked polyurethane (IIp); yield 0.8 g. (80%); d.p. 270°.

1,2-Propylene N-Phenyliminocarbonate (III).—To 6.0 g. of sodium 1,2-propyleneglycolate suspended in 30 ml. of dry benzene was added with vigorous stirring 8.0 g. of phenyl imidophosgene dissolved in 40 ml. of dry benzene. The reaction mixture was refluxed for 2 hr. with continuous stirring, and then poured into water. The benzene layer was separated and washed twice with water. The solution was dried with calcium chloride and after removal of benzene, the distillation gave 1,2-propylene N-phenyliminocarbonate (III); yield 5.6 g. (64%), b.p. 121–123°/0.1 mm.

Anal. Calcd. for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.24; N, 7.91. Found: C, 67.50; H, 6.25; N, 7.74.

Polymerization of III.—To 1.0 g. of III was added a catalytic amount of boron trifluoride. After the iminocarbonate was kept at room temperature for 15 hr., it solidified to give poly(1,2-propylene N-phenylcarbamate) (IIIp), and the polymer was reprecipitated from chloroform–ether; yield 0.9 g. (90%), m.p. 96–99°, $[\eta]^{30°}_{\mathrm{DMF}}$ 0.09.

Reaction of Phenyl Isocyanate with 1-Bromopropanol-2.—A solution of 1.2 g. of phenyl isocyanate, 1.3 g. of 1-bromopropanol-2, and a catalytic amount of boron trifluoride in 30 ml. of ether was refluxed for 5 hr. The distillation gave β-brom-α-methylethyl *N*-phenylcarbamate (IV); yield 2.2 g. (85%), b.p. 134–136°/1 mm., $n^{20°}_{D}$ 1.4884.

Anal. Calcd. for $C_{10}H_{12}BrNO_2$: C, 46.53, H, 4.65; N, 5.42. Found: C, 46.16; H, 4.84; N, 5.16.

Reaction of III with Hydrogen Bromide.—A solution of 1.8 g. of III in 10 ml. of dry ether was saturated with hydrogen bromide and the solution was refluxed for 10 min. The distillation gave β-bromo-α-methylethyl *N*-phenylcarbamate; yield 2.2 g. (85%), b.p. 134–135°/1 mm., $n^{20°}_{D}$ 1.4880.

Anal. Calcd. for $C_{10}H_{12}BrNO_2$: C, 46.53; H, 4.65; N, 5.42. Found: C, 47.09; H, 4.84; N, 5.23.

The infrared spectra of this compound was identical with that of the authentic sample (IV) obtained from the above mentioned reaction of phenyl isocyanate and 1-bromopropanol-2.

Dimethylketene Ethylene Acetal (V).—This substance was prepared according to the method of McElvain and Aldridge[5]; b.p. 149–150°/756 mm., n^{18}_{D} 1.4450 (reported[5] b.p. 153.1–153.3/741 mm., n^{25}_{D} 1.4540). The infrared absorption bands are 1745 cm.$^{-1}$ (s), 1170 (s), 1140 (s), 1040 (s), and 960 (ms).

Polymerization of V.—To 1.0 g. of V was added a catalytic amount of boron trifluoride at room temperature. It polymerized vigorously with evolution of heat. The mixture was then heated and kept at 80° for 1 hr. It was washed with petroleum ether and dried in vacuum at 80° for 1 hr. The resulting polymer was a viscous material. Its infrared absorption bands are at 1735 cm.$^{-1}$ (s), 1250–1100 (s) broad, and 1045 (m).

2-Phenyliminooxazolidine (VI).[6]—Twenty grams of N-(β-chloroethyl)-N′-phenylurea was refluxed with 200 ml. of water for 15 min. After cooling, the solution was neutralized with saturated sodium carbonate. The precipitate was recrystallized from alcohol and water, and 11.0 g. (68%) of VI was obtained, m.p. 119–120°.

Bulk Polymerization of VI.—By a similar method to that of polymerization of ethylene N-phenyliminocarbonate (I), 1 g. of VI was polymerized in the presence of various acidic catalyst as shown in Table III. The resulting polymer was reprecipitated from alcohol–water. Its infrared absorption bands are at 3380 cm.$^{-1}$ (s), 1655(s), 1602 (s), 1550 (s), 1310 (m), 750 (s), and 690 (s).

Anal. Calcd. for $(C_9H_{10}N_2O)_n$; C, 66.65; H, 6.22; N, 17.27. Found: C, 65.41; H, 6.32; N, 16.42.

TABLE III

BULK POLYMERIZATIONS OF 2-PHENYLIMINO OXAZOLIDINE (VI) AT 130–140°

Catalyst	Reaction time, hrs.	Poly(ethylene-N-phenylurea) Yield, %	M.p.	$[\eta]^{30°}_{\mathrm{DMF}}$
Boron trifluoride	10	54	75–80	0.04
Titanium chloride	10	63	70–74	.04
Sulfuric acid (96%)	10	51	63–65	
Aluminum chloride	10	47	60–62	
Phosphorus pentoxide	10	22	65–68	
No catalyst	10	5	61–63	

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(5) S. M. McElvain and C. L. Aldridge, *J. Am. Chem. Soc.*, **75**, 3995 (1953).

(6) S. Gabriel and R. Stelzner, *Ber.*, **28**, 2929 (1895).