The Synthesis and Ring-opening Polymerization of N-Substituted 2-Iminotetrahydrofurans

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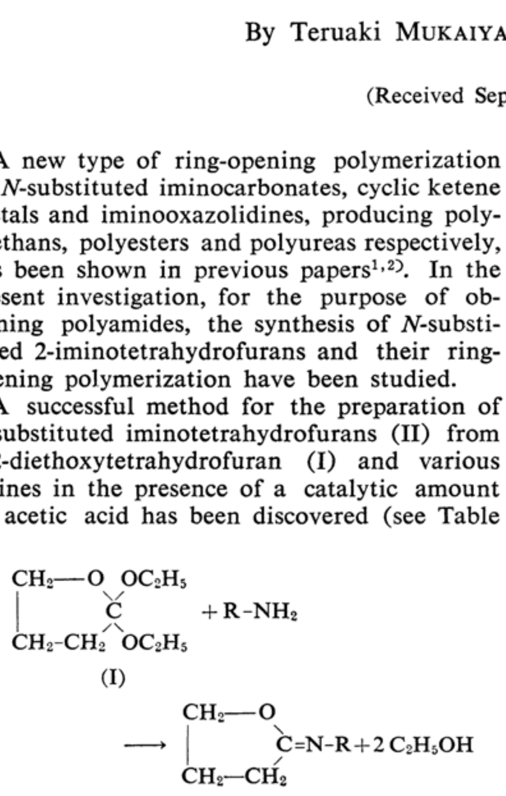
A new type of ring-opening polymerization of *N*-substituted iminocarbonates, cyclic ketene acetals and iminooxazolidines, producing polyurethans, polyesters and polyureas respectively, has been shown in previous papers[1,2]. In the present investigation, for the purpose of obtaining polyamides, the synthesis of *N*-substituted 2-iminotetrahydrofurans and their ring-opening polymerization have been studied.

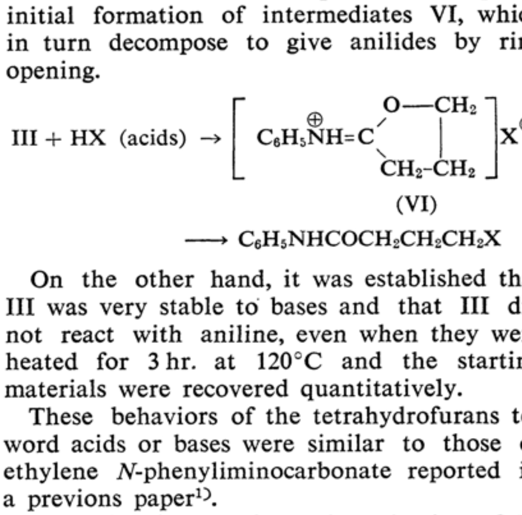
A successful method for the preparation of *N*-substituted iminotetrahydrofurans (II) from 2, 2-diethoxytetrahydrofuran (I) and various amines in the presence of a catalytic amount of acetic acid has been discovered (see Table I).



The highest yield (85%) of 2-phenyliminotetrahydrofuran (V) was obtained when compound I was treated with one equivalent of aniline for 30 min. at 120°C in the presence of a catalytic amount of acetic acid (run 2, Table II). The yield of 2-phenyliminotetrahydrofuran decreased upon prolonged heating because of the polymerization of the tetrahydrofuran produced (run 3, Table II).

It was shown that these tetrahydrofurans were quite sensitive to acidic substances and reacted with hydrogen chloride and benzoic acid to give γ-chlorobutyranilide (IV) and γ-benzoxybutyranilide (V) respectively in good yields.

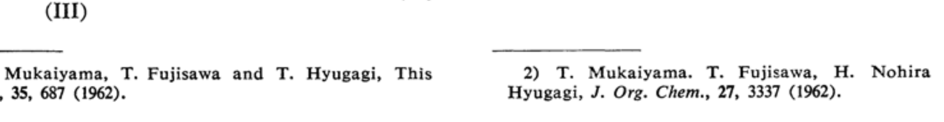
These reactions seem to proceed through an initial formation of intermediates VI, which in turn decompose to give anilides by ring opening.



On the other hand, it was established that III was very stable to bases and that III did not react with aniline, even when they were heated for 3 hr. at 120°C and the starting materials were recovered quantitatively.

These behaviors of the tetrahydrofurans toword acids or bases were similar to those of ethylene *N*-phenyliminocarbonate reported in a previons paper[1].

Next, the ring-opening polymerization of *N*-substituted 2-iminotetrahydrofurans was attempted in the presence of a catalytic amount of boron trifluoride etherate. This catalyst



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[1] T. Mukaiyama, T. Fujisawa and T. Hyugagi, This Bulletin, 35, 687 (1962).

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

TABLE I. THE SYNTHESIS OF *N*-SUBSTITUTED 2-IMINOTETRAHYDROFURANS FROM THE REACTION OF 2,2-DIETHOXYTETRAHYDROFURAN WITH VARIOUS AMINES

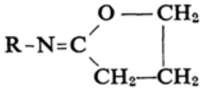
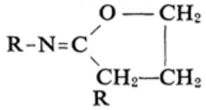
Run	Amine	Reaction conditions			*N*-Substituted 2-iminotetrahydrofurans 			
		Time min.	Temp. °C	Catalyst	R	Yield, %	B. p., °C	mmHg
1	3,4-Dichloroaniline	10	120	None	3,4-Dichlorophenyl-	70	141～142	0.4
2	*p*-Chloroaniline	20	115	Acetic acid	*p*-Chlorophenyl-	72	124～125	0.4
3	*o*-Chloroaniline	20	115	Acetic acid	*o*-Chlorophenyl-	70	145～146	4
4	Aniline	30	120	Acetic acid	Phenyl-	85	128	2
5	*p*-Anisidine	25	125	Acetic acid	*p*-Methoxyphenyl-	80	155	2
6	*o*-Anisidine	20	115	Acetic acid	*o*-Methoxyphenyl-	70	168	5
7	*p*-Toluidine	15	115	Acetic acid	*p*-Methylphenyl-	65	141	3
8	*o*-Toluidine	15	115	Acetic acid	*o*-Methylphenyl-	70	133	4
9	Cyclohexylamine	420	120	Acetic acid	Cyclohexyl-	45	137	27
10	Benzylamine	30	120	Acetic acid	Benzyl-	75	126～127	3
11	*n*-Hexylamine	680	120	Acetic acid	*n*-Hexyl-	30	65	27

TABLE II. THE EFFECT OF THE REACTION TIME

Run	I g.	Aniline g.	Reaction conditions		Starting materials recovered, g.	2-Phenyliminotetrahydrofuran g.	Polymer obtained g.
			Time, min.	Temp., °C			
1	6	3.6	10	120	3	3(50%)	trace
2	6	3.6	30	120	—	5.1(85%)	0.5
3	6	3.6	70	120	—	2.8(47%)	3.0

TABLE III. BULK POLYMERIZATION OF *N*-SUBSTITUTED 2-IMINOTETRAHYDROFURANS

Run	Reactant  R	Polymerization conditions		Yield %	Properties of polymer	
		Time hr.	Temp. °C		Softening point °C	$[\eta]^{30°}_{\text{chloroform}}$
1	3,4-Dichlorophenyl-	7	60～70	95	60	0.05
2	*o*-Chlorophenyl-	5	60～70	85	90	0.11
3	*p*-Chlorophenyl-	2	80～90	85	65	0.09
4	Phenyl-	72	Room temp.	80	105	0.12
5	*o*-Methylphenyl-	6	65	80	60	0.13
6	*p*-Methylphenyl-	6	65	55	60	0.12
7	Benzyl-	7	90～100	50	40	0.10
8	Cyclohexyl-	7	90～100	50	62	—
9	*n*-Hexyl-	7	90～100	5	—	—

was chosen because it was most effective for the ring-opening polymerization of 2-iminocyclic carbonates, which resemble *N*-substituted 2-iminotetrahydrofurans in structure. The results are listed in Table III.

It is also noted that the polymerization of *N*-substituted 2-iminotetrahydrofurans was promoted by heating, even in the absence of a catalyst.

The polymeric substances obtained by this experiment show a weak N–H absorption at 3350～3450 cm^{-1} and a strong carbonyl absorption at 1650 cm^{-1} but no cyclic ether absorption band at 1170～1180 cm^{-1}, which is present in all the monomers.

A reasonable path by which *N*-substituted 2-iminotetrahydrofurans are converted into polyamides can be the cationic polymerization mechanism proposed in the case of cyclic iminocarbonates[2].

An interesting feature regarding ring-opening polymerization in general is the relationship between ring strain and polymerizability. The successful result for the ring-opening polymerization of tetrahydrofuran suggests that the ring strain considered in tetrahydrofuran facilitates the polymerization[3]. However, no polymerization of γ-butyrolactone has ever

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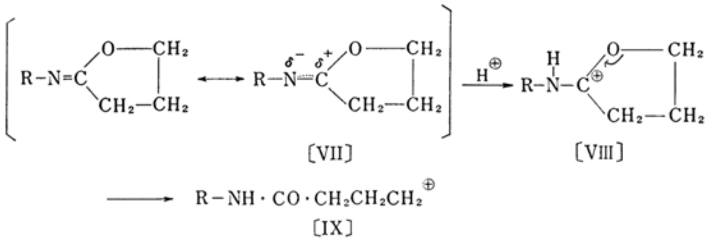
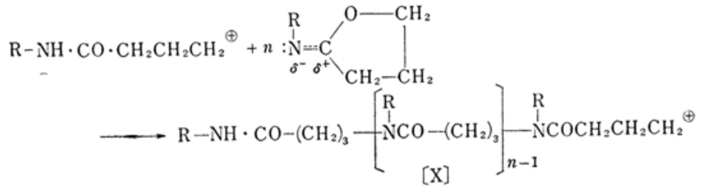
[3] E. L. Muetterties, U. S. Pat. 2856370 (Oct. 14, 1958).

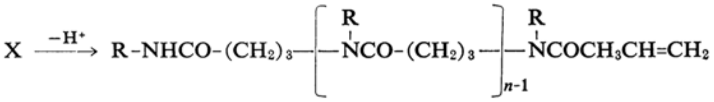
Initiation



Propagation



Termination



$$X \xrightarrow{-H^+} R\text{-}NHCO\text{-}(CH_2)_3\text{—}\left[\text{—}\overset{R}{N}CO\text{-}(CH_2)_3\text{—}\right]_{n-1}\text{—}\overset{R}{N}COCH_3CH{=}CH_2$$

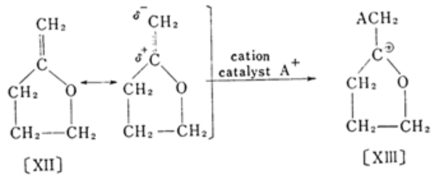
been discovered because the strain is relieved by the introduction of the exo double bond[4].

The fact that *N*-substituted 2-iminotetrahydrofurans which also possess an exo double bond stabilizing the tetrahydrofuran ring are readily polymerized in the presence of cationic catalysts may be because of the basic nature of the imino group, which easily forms a reactive intermediate VIII with the catalyst.

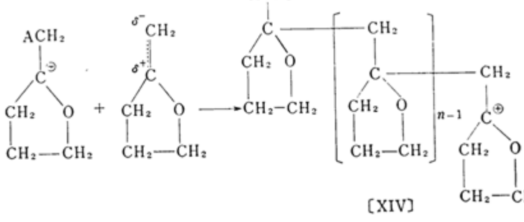
Although *N*-aromatic substituted compounds were readily converted into corresponding polymers, as is indicated in Table III, even under more vigorous conditions, the polymerization of *N*-aliphatic substituted compounds took a long time and their yields were poor. This leads to the conclusion that the step of ring-opening in forming IX from VIII plays a predominant role in this polymerization because the C–O bond fission is facilitated by the introduction of electron-withdrawing aromatic groups.

This type of polymerization was extended further to 2-methylene tetrahydrofuran XII, which also possesses the structural possibility of ring-opening polymerization. When the polymer obtained from the polymerization of XII in the presence of boron trifluoride etherate was examined by means of its infrared spectrum, a strong absorption band attributable to ether linkage (1030 cm^{-1}) was observed. The expected carbonyl band (1700 cm^{-1}) and C=C band (1640 cm^{-1}) were also observed, but they were so weak that the structure of the polymer is assumed to consist of poly cyclic ether, not of poly ketone. This indicates that the polymerization occurs mainly by means of vinyl type ones and that the following mechanism can be suggested:

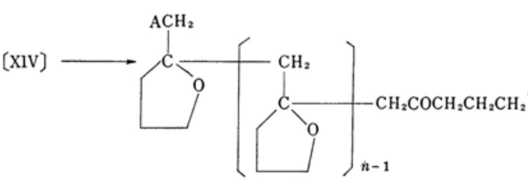
Initiation



Propagation



Termination



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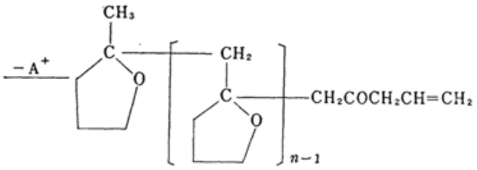
[4] H. C. Brown, J. H. Brewstead and H. Shechter, *J. Am. Chem. Soc.*, **76**, 467 (1954).



From the results obtained by the polymerizations of those tetrahydrofurans possessing a C=N or C=C exo double bond, it can be said that the ring strain of these tetrahydrofurans is not so large that the compound possessing the structural possibility of vinyl type polymerization does not give raise to ring opening.

In conclusion, ring opening polymerization took place when *N*-substituted 2-iminotetrahydrofurans were treated with acidic catalysts, but this type of ring-opening polymerization was scarcely observed in the case of 2-methylenetetrahydrofuran.

Experimental

2, 2-Diethoxytetrahydrofuran. — This compound was prepared according to the method of Meerwein[5].

Preparation of 2-Phenyliminotetrahydrofuran.— A mixture of 8.0 g. of 2,2-diethoxytetrahydrofuran, 4.7 g. of aniline, and 2 drops of glacial acetic acid was heated at 120°C for 30 min. After the removal of the alcohol under reduced pressure, 2-phenyliminotetrahydrofuran was distilled as quickly as possible; yield, 6.8 g. (85%); b. p., 128°C/2 mmHg.

In a similar way, 2-(3,4-dichlorophenyl)-, 2-(*p*-chlorophenyl)-, 2-(*o*-chlorophenyl)-, 2-(*p*-methylphenyl)-, 2-(*o*-methylphenyl)-, 2-(*p*-methoxyphenyl)-, 2-(*o*-methoxyphenyl)-, 2-cyclohexyl-, 2-benzyl-, and 2-*n*-hexyliminotetrahydrofuran were prepared from 2, 2-diethoxytetrahydrofuran and corresponding amines.

2-(3, 4-Dichlorophenyl)-iminotetrahydrofuran
Found: N, 6.01. Calcd. for $C_{10}H_9ONCl_2$: N, 6.09%.

2-(*p*-Chlorophenyl)-iminotetrahydrofuran
Found: N, 7.32. Calcd. for $C_{10}H_{10}ONCl$: N, 7.19%.

2-(*o*-Chlorophenyl)-iminotetrahydrofuran
Found: N, 7.42. Calcd. for $C_{10}H_{10}ONCl$: N, 7.19%.

2-Phenyliminotetrahydrofuran
Found: N, 8.42. Calcd. for $C_{10}H_{11}ON$: N, 8.69%.

2-(*p*-Methoxyphenyl)-iminotetrahydrofuran
Found: N, 7.21. Calcd. for $C_{11}H_{13}ON$: N, 7.33%.

2-Cyclohexyliminotetrahydrofuran
Found: N, 8.14. Calcd. for $C_{10}H_{16}ON$: N, 8.38%.

2-Benzyliminotetrahydrofuran
Found: N, 7.76. Calcd. for $C_{11}H_{13}ON$: N, 7.99%.

Bulk Polymerization of *N*-Substituted 2-Iminotetrahydrofurans.—About 1.0～2.0 g. of *N*-substituted 2-iminotetrahydrofurans were kept under the condition shown in Table III in the presence of a catalytic amount of boron trifluoride etherate. Polymer obtained were reprecipitated from chloroform-petroleum benzin (boiling range 50～90°C).

Reaction of 2-Phenyliminotetrahydrofuran with Hydrogen Chloride.—Dry hydrogen chloride was passed into a solution of 1.4 g. of 2-phenyliminotetrahydrofuran in 5 ml. of dry benzene at 60～70°C for 15 min. On evaporation of the benzene, crude γ-chlorobutyranilide was obtained and recrystallized from ether-ligloin; yield, 1.2 g. (70%); m. p., 69～70°C. This compound was identical in all respects with the authentic sample.

Reaction of 2-Phenyliminotetrahydrofuran with Benzoic Acid.—A solution of 1.4 g. of 2-phenyliminotetrahydrofuran and 1.0 g. of benzoic acid in 5 ml. of dry benzene was refluxed for 1 hr., and then the benzene was removed. γ-Benzoxybutyranilide was obtained and recrystallized from ether; yield, 60%; m. p., 132～134°C. Found: N, 4.78. Calcd. for $C_{17}H_{17}O_3N$: N, 4.91%.

Preparation of 2-Methylenetetrahydrofuran.— This was prepared according to the method of Paul and Tchelitcheff[6].

Bulk Polymerization of 2-Methylenetetrahydrofuran.—2.0 g. of 2-methylenetetrahydrofuran was kept at 100～110°C for 1 hr. in the presence of a catalytic amount of boron trifluoride etherate. The polymer obtained was reprecipitated from ether-acetone; yield, 40%. Softening point, 62°C (m. p., 62～67°C). $[\eta]^{30°}_{\text{chloroform}}$ 0.1.

Summary

Various *N*-substituted 2-iminotetrahydrofurans are prepared from 2, 2-diethoxytetrahydrofuran and corresponding amines.

N-Substituted 2-iminotetrahydrofurans give *N*-substituted polyamides by ring-opening polymerization when treated with a catalytic amount of boron trifluoride etherate.

On the other hand, 2-methylenetetrahydrofuran undergoes mainly a vinyl-type polymerization.

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[5] H. Meerwein, P. Borner et al., *Chem. Ber.*, **89**, 2060 (1956).

[6] M. R. Paul and S. Tchelitcheff, *Bull. soc. chim. France*, **1950**, 520.