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Syntheses of Some Polymers Containing Cyclopropane Rings in the Main Chain. II*.

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SUMMARY:

Polyurethanes, polyureas, polycarbodiimide, and polyamines containing cyclopropane ring in the main chains were prepared, using 1,2-cyclopropane diisocyanate, 1,2-diaminocyclopropane, 1,2-cyclopropane diacylisocyanate, 1,2-bisaminomethyl-cyclopropane, or 1,2-bisiodomethyl-cyclopropane as one component. Polyurethanes and polyureas were prepared by usual methods. Polycarbodiimide was synthesized according to the method of CAMPBELL, where 1-ethyl-3-methyl-3-phospholene oxide was used as polymerization catalyst. Polyamines were obtained by applying the novel method which was reported by KLEBE. Some polymers and their films showed good technological properties.

ZUSAMMENFASSUNG:

Einige neue Polyurethane, Polyharnstoffe, Polycarbodiimide und Polyamine, welche den Cyclopropanring in ihrer Hauptkette enthalten, wurden aus 1,2-Cyclopropandiisocyanat, 1,2-Diaminocyclopropan, 1,2-Cyclopropan-diacylisocyanat, 1,2-Bisaminomethyl-cyclopropan bzw. 1,2-Bisjodmethyl-cyclopropan als eine Komponente dargestellt. Polyurethane und Polyharnstoffe wurden nach den üblichen Verfahren synthetisiert. Zur Darstellung der Polycarbodiimide diente die Methode von CAMPBELL mit 1-Äthyl-3-methyl-3-phospholinoxyd als Katalysator. Die Polyamine wurden nach der Methode von KLEBE dargestellt. Einige Polymere und die daraus gewonnenen Filme zeigen ausgezeichnete technische Eigenschaften.

Introduction

The syntheses of polyesters, polyamides, and polyamines containing the cyclopropane ring in the main chain have been reported in the previous paper[1] and some of these polymers showed good properties.

In this paper, the syntheses of polyurethanes, polyureas, polycarbodiimide and polyamines, using 1,2-cyclopropane diisocyanate, 1,2-diaminocyclopropane, 1,2-cyclopropane diacylisocyanate, 1,2-bisaminomethyl-cyclopropane, or 1,2-bisiodomethyl-cyclopropane as a monomer component, are reported.

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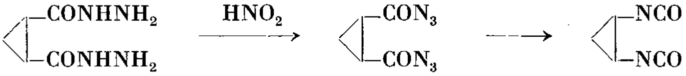
*) Studies on the Small Ring Compounds, VI.

a) *Synthesis of 1,2-Cyclopropane Diisocyanate*

The 1,2-cyclopropane diisocyanate was synthesized applying the method of Curtius as described below.



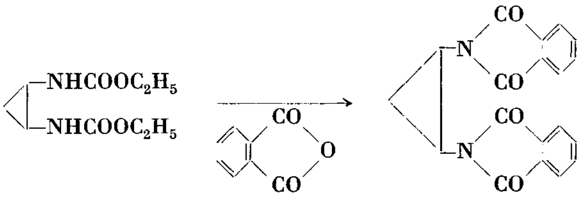
It has been known that in the alkylene diisocyanate, when the numbers of methylene groups between the two isocyanate groups are small the diisocyanate becomes very unstable, for example, the ethylene diisocyanate easily changes to white polymer$^{2)}$. In the 1,2-cyclopropane diisocyanate, the *trans* isomer was moderately stable and could be purified by distillation, while the *cis* isomer was very unstable and, on heating, turned into polymer-like substance.

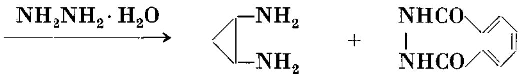
Some stereochemical interests were found in the Curtius rearrangement of 1,2-cyclopropane dicarboxylic azide. In the Curtius rearrangement, the optical activity of starting compounds are always retained. However it has been reported that in the case of the rearrangement of geometrical isomers the configurations are not necessarily retained. For instance, both the *trans*- and *cis*-1,3-cyclohexane dicarboxylic azides gave the same urethane.

Similar situations have been observed in the rearrangement of some other geometrical isomers, with exception of the 1,2-cyclobutane dicarboxylic acid derivative$^{3,4)}$. Interestingly, it was found that in the rearrangement of 1,2-cyclopropane dicarboxylic azide studied here the geometrical configuration was retained.

b) *Synthesis of 1,2-Diaminocyclopropane*

The diaminocyclopropane was first expected to be obtained by direct hydrolysis of the urethane derived from the diisocyanate, but this urethane could be hydrolyzed only under drastic conditions, where the occurrence of the decomposition of diamine was inevitable. The catalyzed hydrogenation of urethane was not suitable to prepare the diamine either. Therefore the *trans* isomer of this diamine was synthesized according to the following reaction scheme.

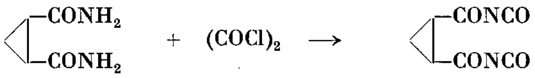




However, an attempt to prepare the *cis* isomer by the same method was unsuccessful. This would be attributed to the difficulty of the formation of the bisphthalimide compound due to the steric hindrance of *cis* configuration. A very small amount of *cis* diamine could be obtained by hydrolysis of the urethane in aqueous barium hydroxide.

c) *Synthesis of 1,2-Cyclopropane Diacylisocyanate*

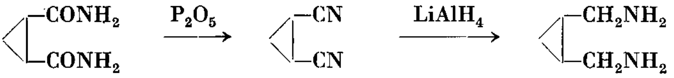
The diacylisocyanate was prepared from the dicarboxamide by treating with oxalyl chloride.



The diacylisocyanate was highly reactive to the atmospheric moisture. The *cis* isomer of the diacylisocyanate was thermally unstable similarly to that of the 1,2-cyclopropane diisocyanate and it was scarcely distilled under reduced pressure without decomposition.

d) *Synthesis of 1,2-Bisaminomethyl-cyclopropane*

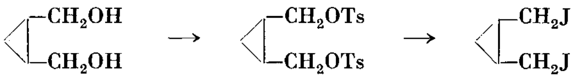
The 1,2-bisaminomethyl-cyclopropane was synthesized according to the usual method of preparing amines.



The dehydration of 1,2-cyclopropane dicarboxamide into the nitrile was performed by using phosphorus pentoxide as dehydrating agent. When phosphorus oxychloride was used, tarry material was the main product. The diamine was obtained by reduction of the nitrile by lithium aluminum hydride. In the BOUVEAULT-BLANC type reduction of the nitrile, the diamine was also formed, but the isolation was very difficult. In the synthesis of the dicarboxamide or nitrile, the configuration of *trans* isomer was retained, while some degree of inversion of *cis* isomer to *trans* isomer was observed.

e) *Synthesis of 1,2-Bisiodomethyl-cyclopropane*

The method of synthesis of the *cis*-1,2-bisiodomethyl-cyclopropane was reported by VOGEL[5)].



The *trans* isomer was also obtained by applying this method.

Table 1. 1,2-Disubstituted Cyclopropanes

	B.p. (°C./mm. Hg)	M.p. (°C.)	Yield (%)
1,2-Cyclopropane diisocyanate	*trans* 46/4	diethyl-urethane 66–68	48
	cis —	127–128	30
1,2-Diamino-cyclopropane	*trans* 80/110	dipicrate 140	40
1,2-Cyclopropane dicarbonitrile	*trans* —	71.5	65
	cis —	52	22
1,2-Cyclopropane diacylisocyanate .	*trans* 90/5	dimethyl-urethane 350	83
	cis —	218	—
1,2-Bisaminomethyl-cyclopropane .	*trans* 75/27	dipicrate 207	20
1,2-Bisiodomethyl-cyclopropane	*trans* —		88.5

f) *Syntheses of Polyurethanes*

The polyurethanes were synthesized by the usual method, that is, by heating of equimolecular mixture of two components, such as, 1,2-cyclopropane diisocyanate or diacylisocyanate and glycols in anisole under nitrogen atmosphere. As the glycol components, tri-, tetra-, and pentamethyleneglycols and *trans*- and *cis*-1,2-dimethylol-cyclopropanes were used. The results are shown in Table 2. In the case of using straight chain glycols, the polyurethanes consisting of longer alkylene chains had better technological properties than that of shorter chains. The *trans*-1,2-dimethylol-cyclopropane gave better polymer than the *cis* isomer. Especially good films were obtained from the polymer prepared from *trans*-1,2-dimethylol-cyclopropane and 1,2-cyclopropane diisocyanate. Since the anisole was found to be a poor solvent the polymerization was carried out also in N-methylpyrrolidone which was a better solvent for the polymer. The obtained polymer, however, was not so good as expected.

g) *Syntheses of Polyureas and Polycarbodiimide*

The polyureas were prepared by general method using anisole or m-cresol as solvent. The used diamines were hexamethylenediamine and piperazine. The polyurea consisting of *cis* component was tried to prepare from the corresponding urethane, because the *cis*-diisocyanate could not be isolated as mentioned above. The results are indicated in Table 3.

Table 2. Polyurethanes; yield 100%

Diisocyanate	Glycol	M.p. (°C.)	η_{sp}/c (g./100 ml.)[d]
trans IC[a]	trimethylene glycol	∼170	0.20[f]
	tetramethylene glycol	∼180	0.44[f]
	pentamethylene glycol	∼135[g]	0.20
	pentamethylene glycol	∼170	0.49
	trans M[b]	∼125[g]	0.21
	trans M[b]	∼210	1.60[e]
	cis M[b]	∼175	0.34
trans AIC[c]	tetramethylene glycol	∼226	0.17[h]
	pentamethylene glycol	∼250[g]	0.11[h]
	pentamethylene glycol	∼215	0.22[h]
	trans M[b]	∼205	0.33[h]
	trans M[b]	∼245[g]	0.15[h]

[a] IC-1,2-Cyclopropane diisocyanate. [b] M-1,2-Dimethylol-cyclopropane.

[c] AIC-1,2-Cyclopropane diacylisocyanate.

[d] Measured in N-methyl-2-pyrrolidon at 30 °C. unless otherwise mentioned.

[e] Measured in DMSO. [f] Measured in DMF.

[g] Polymerized in N-methyl-2-pyrrolidon. [h] η_{sp}/c: c = 0.25 g./100 ml.

Table 3. Polyureas and Polycarbodiimide

Diisocyanate	Diamine	Reaction solvent	Yield (%)	M.p. (°C.)	η_{sp}/c (c = 0.25 g./100 ml., 30 °C.)
trans IC[a]	hexamethylene diamine	anisole	20	∼180	0.53 in formic acid
trans IC	piperazine	*m*-cresol	—	∼260	0.66 in formic acid
cis-diurethan	piperazine	—	—	∼280	insoluble
trans IC	—	benzene	—	∼240	insoluble[b]
trans IC	—	benzene + DMSO (9:1)	—	∼300	insoluble[b]

[a] Abbreviations see Table 2.

[b] 1-Ethyl-3-methyl-3-phospholene oxide was used as catalyst.

Campbell reported the syntheses of polycarbodiimides from the diisocyanates by heating with suitable catalyst, such as 1-ethyl-3-methyl-3-phospholene oxide, in an inert solvent[6]. The Campbell method was applied to prepare the polycarbodiimide from 1,2-cyclopropane diisocyanate. The obtained results are also showed in Table 3.

The polymer, thus prepared, was insoluble in any solvent. According to CAMPBELL's report, when a small amount of dimethyl sulfoxide is existent in this polymerization system the formed polymer becomes soluble in some solvents. However, the polymer derived from 1,2-cyclopropane diisocyanate by applying this method was still insoluble.

h) *Syntheses of Polyamides*

The polyamides were prepared by interfacial polycondensation method as reported in the previous paper. The used acyl chlorides were *trans*-1,2-cyclopropane dicarboxylic chloride, sebacyl chloride and isophthalyl chloride. The results are given in Table 4. The polyamide obtained from *trans*-1,2-diaminocyclopropane and sebacyl chloride showed good properties and gave good film.

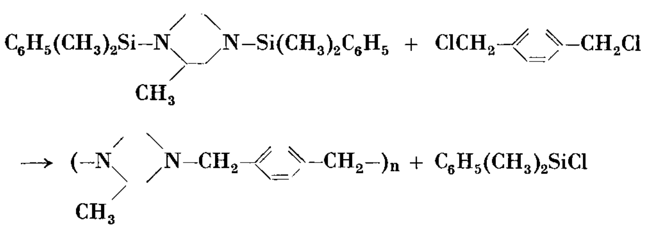
Table 4. Polyamides

Diamine	Acid chloride	Yield (%)	M.p. (°C.)	η_{sp}/c (c = 0.25 g./100 ml., 30 °C., in formic acid)
trans A[a]	*trans* C[b]	40	~285	0.20
	sebacic acid	60	~220	1.65
	isophthalic acid	50	~250	0.25
trans MA[c]	*trans* C[b]	22	~220	0.34
	sebacic acid	46	~223	0.42
	isophthalic acid	36	~220	0.24

[a] A-1,2-Diaminocyclopropane. [b] C-1,2-Cyclopropane dicarboxylic acid.
[c] MA-1,2-Bisaminomethyl-cyclopropane.

i) *Syntheses of Polyamines*

KLEBE[7] reported a novel method for the syntheses of some polyamines according to the following reaction scheme.



This method was applied to prepare a polyamine from 1,2-bisiodomethylcyclopropane. The reduced viscosities (in water, c = 0.25 g./100 ml., 30 °C.) of the obtained polyamines are 0.20 for *trans* isomer and 0.04 for *cis* isomer.

Experimental

a) *Synthesis of 1,2-Cyclopropane Diisocyanate*

Under stirring, 31.6 g. (0.2 mole) of dimethyl-1,2-cyclopropane dicarboxylate (*trans*, bp.$_{16}$ 82–84 °C.; *cis*, bp.$_{12}$ 102 °C.) was added dropwise during 1 hr. to 31.6 g. (0.51 mole) of 80% hydrazine hydrate at 120 °C. After additional heating for 20 min., the reaction mixture was cooled and the separated dihydrazide was filtered and treated with boiling alcohol during 5 min. The yields were 95% for *trans* isomer (m.p. 207–211 °C.) and 80% for *cis* isomer (m.p. 167–178 °C.).

$C_5H_{10}N_4O_2$	Calcd.	C 37.97	H 6.33	N 35.44
	Found for *trans*	C 38.27	H 6.54	N 35.69
	Found for *cis*	C 37.72	H 6.54	N 35.58

Under vigorous stirring a solution of 8 g. of sodium nitrite in 20 ml. of water was added to a ice-cooled solution of 8 g. (0.05 mole) of the above obtained dihydrazide and 12 g. of 35% hydrochloric acid in 50 ml. of water at 5 °C. After addition, the toluene layer was separated, dried and then heated at 120 °C. After the evolution of nitrogen gas ceased, the toluene solution was distilled in vacuo to yield the diisocyanate, bp.$_4$ 46 °C. for *trans* isomer. The yields were 48% for *trans* isomer and 30% for *cis* isomer. Diethyl urethanes were derived from these diisocyanates; *trans*, m.p. 66–68 °C.; *cis*, m.p. 127–128 °C.

$C_9H_{16}N_2O_4$	Calcd.	C 49.99	H 7.46	N 12.96
	Found for *trans*	C 50.34	H 7.70	N 13.56
	Found for *cis*	C 50.08	H 7.44	N 12.99

b) *Synthesis of 1,2-Diaminocyclopropane*

A mixture of 33 g. (0.15 mole) of *trans*-diurethane and 97 g. (0.66 mole) of phthalic anhydride was heated during 1 hr. at 230–250 °C. The reaction mixture was then cooled and washed with aqueous solution of sodium bicarbonate. The yield of the *trans*-bis-phthalimide, thus obtained, was 57% and its melting point was 248 °C. (recrystallized from dioxane).

$C_{19}H_{14}N_2O_4$	Calcd.	C 68.67	H 3.64	N 8.43
	Found	C 68.94	H 3.78	N 8.73

40 g. (0.125 mole) of this bisphthalimide was heated with 15.1 g. (0.241 mole) of 80% hydrazine hydrate in 120 ml. of ethanol during 40 min. The reaction mixture was then cooled and filtered. The filtrate was strongly alkalified and extracted with methylene chloride. The methylene chloride layer was distilled at 80 °C./110 mm. Hg to obtain the *trans*-diamine, the yield being 40%. The dipicrate from this diamine melted at 140 °C.

$C_{15}H_{14}N_8O_{14}$ (dipicrate)	Calcd.	C 33.97	H 2.66	N 21.13
	Found	C 33.46	H 2.99	N 20.97

c) *Synthesis of 1,2-Cyclopropane Diacylisocyanate*

To a suspension of 12.8 g. (0.1 mole) of 1,2-cyclopropane dicarboxamide in 100 ml. of dichloroethane, 32 g. (0.25 mole) of oxalylchloride were added and the reaction mixture was refluxed for 6 hrs. The clear solution thus obtained was distilled to obtain the diacylisocyanate. Bp.$_5$ 90 °C. (*trans* isomer), the yield being 15 g. (83 %). The melting point of the dimethyl urethane derived from the diacylisocyanate was above 350 °C. for *trans* isomer and 218 °C. for *cis* isomer.

$C_9H_{12}N_2O_6$	Calcd.	C 44.26	H 4.85	N 11.47
	Found for *trans*	C 44.48	H 4.84	N 11.70
	Found for *cis*	C 44.39	H 5.00	N 11.49

d) *Synthesis of 1,2-Bisaminomethyl-cyclopropane*

To 750 ml. of a cooled 28 % aqueous solution of ammonia, 85 g. (0.51 mole) of *trans*-1,2-cyclopropane dicarboxylic chloride were added dropwise under stirring. After being stirred for 1 hr., the separated *trans*-1,2-cyclopropane dicarboxamide was filtered, washed with ethanol and dried. The yield was 52.5 g. (81 %), and it melted at 279 °C. (recrystallized from water). The *cis*-1,2-cyclopropane dicarboxamide was prepared by amminolysis of dicarboxylic ester, the yield being 39 %. It melted at 215 °C.

$C_5H_8N_2O_2$	Calcd.	C 46.87	H 6.25	N 21.87
	Found for *trans*	C 46.62	H 6.36	N 21.72
	Found for *cis*	C 47.03	H 6.14	N 22.14

A mixture of 12.8 g. (0.1 mole) of the *trans*-dicarboxamide and 30 g. of phosphorus pentoxide was distilled under reduced pressure (3 mm. Hg) to yield the *trans*-dinitrile, mp. 71.5 °C., yield being 6.0 g. (65 %). The *cis*-1,2-cyclopropane-dicarbonitrile was also obtained by the same method, the yield being 22 %. It melted at 52 °C.

$C_5H_4N_2$	Calcd.	C 65.20	H 4.35	N 30.42
	Found for *trans*	C 65.42	H 4.49	N 30.63
	Found for *cis*	C 64.94	H 4.45	N 30.55

To a stirred suspension of 8 g. (0.21 mole) of $LiAlH_4$ in 300 ml. of dry THF, a solution of 9.2 g. (0.1 mole) of the *trans*-dinitrile in 150 ml. of dry THF was added dropwise at 35–45 °C. After addition, the reaction mixture was heated at 35–45 °C. for additional 2 hrs. and then the excess $LiAlH_4$ was decomposed by water. After the addition of potassium hydroxide and 20 % aqueous solution of sodium potassium tartrate to the reaction mixture, the THF layer was separated and the aqueous layer was extracted twice with THF. The combined THF layer was dried and distilled. The *trans*-1,2-bisaminomethyl-cyclopropane was distilled at 75 °C./27 mm. Hg, the yield being 2 g. (20 %). The dipicrate melted at 207 °C. dec.

$C_{17}H_{18}N_8O_{14}$	Calcd.	C 36.71	H 3.46	N 19.74
	Found	C 36.51	H 3.24	N 20.04

e) *Synthesis of 1,2-Bisiodomethyl-cyclopropane*

The *cis* isomer of 1,2-bisiodomethyl-cyclopropane was prepared according to the method of Vogel. The trans isomer was also obtained by using the same method. The ditosylate of *trans*-1,2-bismethylol-cyclopropane was prepared in 77.5 % yield, the melting point being 78 °C.

$C_{19}H_{22}S_2O_6$	Calcd.	C 55.59	H 5.40
	Found	C 55.68	H 5.46

The yield of *trans*-1,2-bisiodomethyl-cyclopropane was 88.5 %.

f) *Synthesis of Polyurethane*

Under nitrogen atmosphere a solution of 0.977 g. (0.0079 mole) of *trans*-1,2-cyclopropane diisocyanate in 20 ml. of anisole was added with stirring to a boiling solution of 0.820 g. (0.0079 mole) of pentamethylene glycol in 20 ml. of anisole. After refluxing and stirring for 4.5 hrs. the reaction mixture was cooled. The polyurethane prepared was treated with boiling ethanol, dried and purified by reprecipitation using DMF as solvent and methanol as precipitant.

g) *Synthesis of Polyurea and Polycarbodiimide*

1) During 30 min. a solution of 0.930 g. (0.0075 mole) of *trans*-1,2-cyclopropane diisocyanate in 20 ml. of anisole was added dropwise at 0 °C. under nitrogen atmosphere to a solution of 0.871 g. (0.0075 mole) of hexamethylenediamine in 30 ml. of anisole. After the reaction mixture was heated at 70 °C. for 30 min. a small amount of the anisole solution of the diisocyanate was added and then the reaction was carried out at 160 °C. for 30 min. The obtained polymer was treated with boiling ethanol, dried and purified by reprecipitation using *m*-cresol as solvent and methanol as precipitant. In the case of using piperazine as diamine component, *m*-cresol was used as solvent.

2) Under nitrogen atmosphere a mixture of 1.271 g. (0.0148 mole) of piperazine and 3.191 g. (0.0148 mole) of *cis*-diurethane derived from *cis*-diisocyanate was heated at 200 °C. during 3 hrs. The formed ethanol was evaporated under reduced pressure. The obtained polymer was insoluble in any solvents.

3) A solution of 2.9 g. of *trans*-1,2-cyclopropane diisocyanate in 20 ml. of dry benzene containing 2 drops of 1-ethyl-3-methyl-3-phospholene oxide as catalyst was allowed to stand at room temperature for 20 min., and boiled during 2 hrs. The polymer separated from the solution, it was insoluble in any solvent examined.

h) *Synthesis of Polyamide*

Under vigorous stirring, a solution of 2.606 g. (0.0109 mole) of sebacyl chloride in benzene was added to an ice cooled solution of 0.785 g. (0.0109 mole) of *trans*-1,2-diaminocyclopropane, 0.51 g. (0.0221 mole) of sodium hydroxide and 0.5 g. of sodium lauryl sulfate in 100 ml. of water. After stirring for 10 min. the polymer was filtered, washed, dried and purified by reprecipitation using 98% formic acid as solvent.

i) *Synthesis of Polyamine*

A mixture of 4.827 g. (0.015 mole) of *trans*-1,2-bisiodomethyl-cyclopropane, 13.453 g. (0.015 mole) of bis-N,N′-trimethylsilylpiperazine and a small amount of ammonium chloride was heated at 150 °C. under nitrogen atmosphere. After heating for 1 hr. N-methylpyrrolidone was added as solvent and the reaction was continued for additional 4 hrs. The solution was then poured into methanol and the separated polymer was filtered, dried and purified by reprecipitation using water as solvent.

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