

became very viscous or solidified. The tube was then cooled and broken open and the polymer was washed thoroughly with warm water and acetone and dried. The polymerization results are summarized in Table I.

Poly- γ -butyramide from 2-Pyrrolidinone.—In an experiment without cocatalyst, sodium hydride, 0.10 g., was dissolved in 10.0 g. of anhydrous 2-pyrrolidinone with evolution of hydrogen. The resulting solution slowly became turbid. After being kept at room temperature overnight, it gave an 8% yield of poly- γ -butyramide, η_{inh} 0.20 in *m*-cresol.

The polymerization was accelerated strongly by the addition of cocatalysts (0.08–0.25 *M*) including *N*-acyl lactams, acyl halides, acid anhydrides, isocyanates, isothiocyanates, esters or dimethylcyanamide.¹² Other effective substances were nitriles, aromatic nitro compounds (purple color), fluorene, dialkyl amides, and polyhalo aliphatics. Compounds without effect included aromatics, halo aromatics, various salts, amides, lactams, ketones, ethers, sulfones, sulfoxides and amines. Inhibitors at these concentrations included acidic materials like alcohols or phenols. At high concentrations, the "indifferent" materials inhibited polymerization.

In a typical case of cocatalysis, acetic anhydride, 0.10 g., was added to a solution of 0.13 g. of NaH in 6.5 g. of pyrrolidinone. An exothermic reaction ensued, leading to the rapid formation of a hard white plug of polymer. This was broken into small pieces and extracted with water and acetone to give 5.7 g. of poly- γ -butyramide, η_{inh} 0.88 in *m*-cresol. Yields never exceeded 75–85% in such experiments, presumably because residual monomer became embedded in a matrix of polymer at these conversions.

Trapping Anionic Intermediate with Methyl *p*-Toluenesulfonate.—Sodium hydride, 0.75 g., was dissolved in 50 ml. of anhydrous pyrrolidinone. With cooling, was added 5.0 g. of methyl *p*-toluenesulfonate, resulting in the precipitation of sodium *p*-toluenesulfonate. After 30 minutes, the mixture was distilled in a spinning band column. With a pot temperature of 150°, no distillation occurred, showing that no pyrrolidine or *N*-methylpyrrolidine had formed. Vacuum distillation gave 2.21 g. (71.3%) of *N*-methylpyrrolidinone, n_{D}^{27} 1.4679 (authentic material n_{D}^{27} 1.4676). This result is consistent with the view that the anion present is always that of pyrrolidinone.

Poly- ϵ -caproamide from 2-Oxohexamethylenimine.—2-Oxohexamethylenimine, 25.0 g., and sodium hydride, 0.60 g., were placed in a polymer tube which was evacuated and filled with nitrogen several times. The lactam then was melted and the sodium hydride dissolved with evolution of hydrogen. *N*-Acetylcaprolactam, 0.33 g., was added. The tube was shaken thoroughly and placed in a 139° vapor bath. The contents solidified quickly. After 30 minutes, the tube was cooled, and opened. The polymer was ground up, extracted with hot water, and dried to give 18.9 g. (74.7%) of polymer, η_{rel} 26.77 in formic acid. Other similar runs gave polymer in up to 80% yield, η_{inh} 1.0 in *m*-cresol. Blank experiments without the *N*-acetylcaprolactam gave no polymer below 150°.

At 202° a mixture of 4.0 g. of 2-oxohexamethylenimine, 2.0 ml. of 2-pyrrolidinone, 0.15 g. of NaH and 0.054 g. of *N*-acetylcaprolactam polymerized smoothly over a period of two hours. The polyamide was pure poly- ϵ -caproamide.

Anal. Calcd. for C₆H₁₁ON: N, 12.4. Found: N, 12.3.

Poly- β -alanine from 1,5-Diazacyclooctane-2,6-dione.—The dilactam, 0.85 g., was heated with two drops of water at 218° for 2.3 hours. The product was cooled, washed with water and dried, giving 0.30 g. polymer, η_{inh} 0.21 in sulfuric acid, m.p. 350° on a heated bar.²⁷

Anal. Calcd. for C₈H₅ON: C, 50.7; H, 7.1; N, 19.7. Found: C, 49.1; H, 6.5; N, 17.6.

Poly-7-heptanethioamide from 2-Heptamethylenimine-thione.—The thiolactam was heated at 250° for 2 hours with sodium in the ratio of 30:1 to give a rubbery, tough polymer, m.p. 235°. Water at 180° for 120 hours gave a similar product, as did heating with sodium at 170° for 120 hours.

Poly-8-octanethioamide from 2-Octamethylenimine-thione.—The thiolactam was heated at 180° for 48 hours with water or sodium in the ratios 10:1 and 20:1, respectively. The polythioamide was a brown rubbery solid which hardened somewhat on exposure to air.

(27) D. S. Breslow, G. E. Hulse and A. S. Matlock, *THIS JOURNAL* **79**, 376° (1957), give m. p. 340°.

WILMINGTON 98, DEL.

[CONTRIBUTION FROM THE PIONEERING RESEARCH DIVISION, TEXTILE FIBERS DEPARTMENT, AND THE CENTRAL RESEARCH DEPARTMENT, E. I. DU PONT DE NEMOURS AND CO., INC.]

Polymerization of Cyclic Esters, Urethans, Ureas and Imides

By H. K. HALL, JR., AND A. K. SCHNEIDER

RECEIVED JUNE 30, 1958

The polymerizations of a variety of cyclic esters, urethans, imides, anhydrides and ureas was studied. The 4-, 7- and 8-membered rings polymerized in almost every case, while the polymerizability of 5- and 6-membered rings depended on the class of compound.

The preceding article¹ described the polymerization of a variety of lactams to linear polymers. The present article describes the extension of this work to cyclic esters, urethans, ureas and imides.

The syntheses of the required monomers for the most part followed conventional methods. The experimental details and literature references are given in the Experimental section and in Table II.

Polymerizations were carried out with molten monomer since no useful solvents were found. Polymerization was undertaken at several temperatures between the melting point of the monomer and 250°, at which point decomposition usually became excessive. Sodium or sodium hydride catalyzed the polymerization of lactones, one urethan and one urea. The lactones also could be polymerized by a variety of other catalysts, including

sulfonic acids, tetraisopropyl titanate, litharge, potassium carbonate and water. Tetramethyleneurea could be polymerized by heat alone. No conversion of a cyclic imide to a polymer could be effected.

The results of the polymerization studies are given in Table I, including for completeness the re-

Class of monomer	Polymerizability		Additional references
	5-Ring	6-Ring	
Lactam	+	—	Reference 1
Lactone	—	+	"Collected Papers of W. H. Carothers," Interscience Publishers, Inc., New York, N. Y., 1940
Urethan	Dec.	+	
Urea	+	—	
Imide	—	—	<i>Ibid.</i>
Anhydride	—	—	<i>Ibid.</i>

(1) H. K. Hall, Jr., *THIS JOURNAL*, **81**, 6412 (1959).

sults of previous investigators. Several qualitative conclusions emerge from these findings:

(1) The polymerizability of 5- and 6-membered carbonyl-containing cyclic monomers depends markedly on the class of compound involved. The situation may be summarized as tabulated.

(2) Four-, seven- and eight-membered rings polymerized in almost all cases.

(3) Alkyl or aryl substituents on a ring always decreased polymerizability. This was shown clearly in the series of substituted glycolides I and δ -valerolactones II. In the former case, two methyls could be tolerated, but four methyls or phenyls rendered the monomer unpolymerizable. In the latter case, one *n*-propyl or two methyls were sufficient to stabilize the ring.

TABLE I
POLYMERIZATION OF CYCLIC MONOMERS

Compound	Ring size	Polymerization
Cyclic esters ^a		
Propiolactone ^b	4	+
β -Butyrolactone ^b	4	+
α,α -Bis-(chloromethyl)-propiolactone ^c	4	+
γ -Butyrolactone ^d	5	-
γ -Valerolactone ^d	5	-
Ethylene carbonate ^d	5	-
Tetramethylethylene carbonate ^a	5	-
2,2-Dimethyl-4-phenyl-1,3-dioxolan-5-one ^a	5	-
Lactone of <i>trans</i> -2-hydroxycyclohexaneacetic acid ^a	5	-
δ -Valerolactone ^{c,d,f}	6	++
3,4,5-Trimethoxy- δ -valerolactone ^c	6	+
1,4-Dioxane-2-one ^f	6	+
Glycolide ^d	6	+
Lactide ^d	6	+
1,4-Dithiane-2,5-dione ^g	6	+
Trimethylene carbonate ^d	6	+
Neopentylene carbonate ^a	6	+
Ethylene oxalate ^d	6	+
Propylene oxalate ^d	6	+
3- <i>n</i> -Propyl- δ -valerolactone ^d	6	--
6,6-Dimethyl- δ -valerolactone ^a	6	--
3-Ethyl-1,4-dioxan-2-one ^d	6	--
3,3,6-Trimethyl-1,4-dioxan-2-one ^a	6	--
Tetramethylglycolide ^a	6	--
Tetraphenylglycolide ^a	6	--
ϵ -Caprolactone ^d	7	+
4-Methyl-7-isopropyl- ϵ -caprolactone ^a	7	+
4-Oxa- ϵ -caprolactone ^b	7	-
Lactone of 4-hydroxycyclohexanecarboxylic acid ^m	6	+
<i>cis</i> -Disalicylide ^{a,l}	8	+
Di- <i>o</i> -cresotide ^{a,l}	8	+
Trisalicylide ^{a,l}	12	+
Cyclic imides		
Succinimide ^d	5	--
N-Methylsuccinimide ^a	5	-
N- <i>n</i> -Amylsuccinimide ^a	5	-
Glutarimide ^d	6	-
N-Ethylglutarimide ^a	6	-
N-Phenylglutarimide ^a	6	-
Diglycolimide ^a	6	-

Cyclic urethans and thiourethans

2-Oxazolidinone ^{a,i}	5	-
Benzoxazolone ^a	5	-
Benzthiazolone ^a	5	-
Tetrahydro-2H-1,3-oxazin-2-one ^a	6	+

Cyclic ureas and thioureas

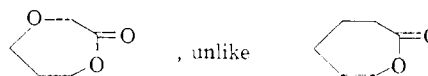
2-Imidazolidinone ^a	5	+
1-Methyl-2-imidazolidinone ^a	5	-
1-Acetyl-2-imidazolidinone ^a	5	-
2-Imidazolidinethione ^a	5	-
Hexahydropyrimidin-2-one ^a	6	-
Tetrahydro-5-methyl-2-(1)- <i>s</i> -triazone ^a	6	--
N,N'-Tetramethyleneurea ^a	7	+
N,N'-Tetramethylenethiourea ^a	7	--
N,N'-(2,2'-Diphenylene)-urea ^a	7	-
N,N'-Dibutyluron ^a	7	-

^a Present investigation. ^b Summarized by H. Zangg in "Organic Reactions," Vol. VIII, John Wiley and Sons, Inc., New York, 1954, p. 326. ^c F. Fichter and A. Beisswenger, *Ber.*, **36**, 1200 (1903). ^d "Collected Papers of W. H. Carothers," Interscience Publishers, Inc., New York, N. Y. ^e H. G. K. Drew and W. N. Haworth, *J. Chem. Soc.*, 775 (1927). ^f E. Hollo, *Ber.*, **61**, 895 (1928). ^g A. Schöberl and G. Wiehler, *Ann.*, **595**, 101 (1955). ^h M. H. Palomaa and U. Toukola, *Ber.*, **66B**, 1629 (1933). ⁱ Oxazolidinone decomposes on heating into ethylenimine and CO₂; see S. Sonnerskog, *Acta Chem. Scand.*, **10**, 467 (1956); J. I. Jones, *Chemistry & Industry*, 1454 (1956). ^j H. Behringer and H. Meier, *Angew. Chem.*, **69**, 106 (1957). ^k C. E. Lowe, U. S. Patent 2,668,162 (1954). ^l A. K. Schneider, U. S. Patent 2,696,481 (1954). ^m H. Batzler and G. Fritz, *Makromol. Chem.*, **14**, 179 (1954). ⁿ R. J. W. Reynolds and E. J. Vickers, Canadian Patent 549,347 (1957).



- 1a, R₁ = R₂ = H; polymerized
 b, R₁ = CH₃, R₂ = H; polymerized
 c, R₁ = R₂ = CH₃; did not polymerize
 d, R₁ = R₂ = C₆H₅; did not polymerize
 11a, R₁ = R₂ = R₃ = H; polymerized
 b, R₁ = *n*-C₃H₇, R₂ = R₃ = H; did not polymerize
 c, R₁ = H, R₂ = R₃ = CH₃; did not polymerize

(4) Substitution of hetero atoms in the ring had in general little effect on the ease of polymerization as compared to the parent monomer. It is known that ring conformations are little affected by the replacement of -CH₂- by -O- or -NH-.² One exception to the above generalization is the fact that the 7-membered ring lactone



fails to polymerize.³ Here the H-H crowding in ϵ -caprolactone may be relieved by substituting -O- for -CH₂-.

These generalizations agree with the results obtained in the polymerization of lactams.¹

With regard to reaction mechanisms, nothing can be said at present except in the case of the ureas. It is possible that the polymerization of te-

(2) D. H. R. Barton and R. C. Cookson, *Quart. Revs.*, **10**, 72 (1956).
 (3) M. H. Palomaa and U. Toukola, *Ber.*, **66B**, 1629 (1933).

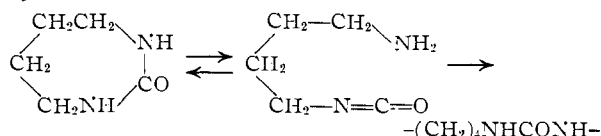
TABLE II
SOURCES OF MONOMERS

Compound	M.p. or b.p. (mm.), °C.	References
2,2-Dimethyl-4-phenyldioxolan-5-one	44	L. F. Audrieth and M. Sveda, <i>Org. Syn.</i> , 20 , 62 (1940), give m.p. 45° Supplied by Dr. M. J. Hogsed
6,6-Dimethyl-δ-valerolactone		
4-Methyl-7-isopropyl-ε-caprolactone	49	A. Baeyer and V. Villiger, <i>Ber.</i> , 32 , 3629 (1899), give m.p. 46–48°
Tetramethylglycolide	79	E. Blaise and P. Bagard, <i>Ann. chim.</i> , [8] 11 , 115 (1907), give m.p. 171°.
Tetraphenylglycolide	197	H. Staudinger, <i>Ber.</i> , 44 , 543 (1911), gives m.p. 193°
cis-Disalicylide	215	W. Baker, W. D. Ollis and T. S. Zeally, <i>J. Chem. Soc.</i> , 201 (1951), give m.p. 234°
Trisalicylide	199	<i>Ibid.</i> , m.p. 200°
cis-Di- <i>o</i> -cresotide	240	W. Baker, B. Gilbert, W. D. Ollis and T. S. Zeally, <i>J. Chem. Soc.</i> , 209 (1951), give m.p. 240°
Imidazolidinone-2	132–133	E. Fischer and H. Koch, <i>Ann.</i> , 232 , 227 (1886), give m.p. 131°
2-Oxohexahydropyrimidine	260–262	<i>Ibid.</i> , m.p. 260°
N,N'-(2,2'-Diphenylene)-urea	315–320	S. von Niementowski, <i>Ber.</i> , 34 , 3330 (1901), gives m.p. 310° Supplied by Dr. R. E. Heckert
N,N'-Dibutyluron		
N-Methylsuccinimide	66	J. Brecht and W. Boeddinghaus, <i>Ann.</i> , 251 , 320 (1888), give m.p. 66°
N-Ethylglutarimide	104 (6.5)	Bodtker, Diss. Leipzig, 1891, Beilstein, H21, 383, gives b.p. 250–260°
N-Phenylglutarimide	142.5–143.5	<i>Ibid.</i> , gives m.p. 144–145°
Diglycolimide		Supplied by Dr. E. T. Darden
2-Oxazolidinone	86–87	A. H. Homeyer, U. S. Patent 2,399,118 (1946), gives m.p. 87–89°

TABLE III
POLYMERIZATIONS—EXPERIMENTAL DETAILS

Monomer, g.	Catalysts, g.	Temp., °C.	Time, hr.	Polymer, g.	η_{inh}	Polymer, m.p., °C.
2-Imidazolidinone, 5.0	NaH, 0.15	148	12.5	3.88	0.15 (H ₂ SO ₄)	>400
	N-Acetylcaprolactam, 0.053					
Tetrahydro-2H-1,3-oxazin-2-one, 4.0	NaH, 0.15	80	2.5	2.27	0.33 (<i>m</i> -cresol)	148
	N-Acetylcaprolactam, 0.053					
N,N'-Tetramethyleneurea, 2.0	240	0.66	1.23	0.72 (H ₂ SO ₄)	>400
4-Methyl-7-isopropyl-ε-caprolactone, 5.0	Na, 0.05	170	2	Thick white hygr. gel
Neopentylene carbonate, 2.0	None	230	1.5	1.47	.06 (<i>m</i> -cresol)	111–112
cis-Disalicylide, 1.0	Lead stearate, 0.0002	230	48	..	.20 (<i>m</i> -cresol)	Softens above 150
Trisalicylide, 2.0	Lead stearate, 0.001	210	88	2.0	.39 (<i>m</i> -cresol)	190
cis-Di- <i>o</i> -cresotide, 0.5	Lead stearate, 0.0002	245	90	0.4

tetramethyleneurea by heat occurs *via* an aminoisocyanate



The 5- and 6-membered ureas dissociate to an aminoisocyanate one-fortieth as rapidly⁴ as the 7-membered compound and their failure to polymerize on heating may be attributed to this slow dissociation.

Acknowledgments.—We are indebted to Drs. N. L. Cox, C. J. Albisetti, E. W. Spanagel and H. E. Winberg for permission to quote unpublished results; to Dr. P. W. Morgan for continued encouragement; and to Messrs. D. G. Preis and R. Schulz for excellent technical assistance.

Experimental

Cyclic Monomers. Tetramethylenethiourea.—The procedure of reference 5 was applied to tetramethylenediamine

to give a 69% yield of crude tetramethylenethiourea. After two recrystallizations from ethyl alcohol the product melted at 177–178° (lit.⁶ m.p. 177°).

Tetramethyleneurea.—The above thiourea was desulfurized with alkaline hydrogen peroxide.⁷ To a suspension of 30.1 g. of tetramethylenethiourea in 405 ml. of 10% aqueous potassium hydroxide at 70° was added with stirring 153 ml. of 30% hydrogen peroxide, keeping the temperature at 70°. The thiourea dissolved. After the addition was complete, sulfur dioxide was passed in, the mixture was filtered, and the filtrate was evaporated to dryness on a steam-bath under aspirator vacuum. Slow sublimation at 100–120° (oil-bath) at 0.2 mm. gave 16.88 g. (64.1%) of crystalline tetramethyleneurea, m.p. 168° when rapidly heated (lit.²⁷ m.p. 162–163).

Adipimide.⁸—Adipamide, 200 g., Eastman Kodak Co., was heated to 250–260°, resulting in copious evolution of ammonia. When gas evolution subsided the pressure was reduced to 60–100 mm. and about 10 g. of water was removed. Further reduction of pressure to 12–17 mm. resulted in distillation of 103.8 g. of a clear sirup boiling at 160–170°. A third fraction, b.p. 180° (3 mm.), solidified in the receiver. Redistillation of the middle fraction through a 10'' packed column gave three liquid fractions after removal of 5 g. of water: 1, b.p. 145–150° (7.5 mm.), 17.2 g., n_D^{20} 1.4672; 2, b.p. 154–160° (7.5 mm.), 22.4 g., n_D^{20} 1.4651; 3, b.p. 156–168° (4 mm.), 24.3 g., n_D^{20} 1.4562.

(4) S. Ozaki, T. Mukaiyama and K. Uno, *THIS JOURNAL*, **79**, 4358 (1957).

(5) C. F. H. Allen, C. O. Edens and J. O. Van Allan, *Org. Syntheses*, **26**, 34 (1946).

(6) E. Strack, *Z. physiol. Chim.*, **130**, 198 (1929).

(7) R. Mecke, *Chem. Ber.*, **89**, 350 (1956).

(8) Synthesis and characterization of this compound was first carried out by Dr. G. W. Rigby of these laboratories.

Fractions 2 and 3 could be precipitated with aqueous ammonia, indicating the presence of adipimide by formation of insoluble adipamide. Cooling of fraction 2 gave a crystalline deposit which was filtered and recrystallized from benzene-petroleum ether to give 2.5 g. of adipimide, m.p. 98°. Polymer was not obtained from this monomer.

Anal. Calcd. for $C_6H_9O_2N$: C, 56.7; H, 7.1. Found: C, 57.1, 57.0; H, 7.4, 7.3.

Tetrahydro-2H-1,3-oxazin-2-one.—To a solution of di-*p*-cresyl carbonate, 24.2 g., in 100 ml. of methylene chloride in a spinning band flask was added 7.51 g. of 3-aminopropanol. No visible reaction occurred. The solvent was evaporated, 0.05 g. of sodium hydride was added, and the flask was attached to the column. A 1 mm. vacuum was applied and heating was begun with an oil-bath. At 180° *p*-cresol distilled smoothly over a one-hour period; 20.5 g., b.p. 70° (1 mm.). The residue was cooled, taken up in 50 ml. of hot ethyl acetate, filtered using decolorizing charcoal and diatomaceous earth and chilled in solid carbon dioxide-acetone. It crystallized well and was filtered rapidly while still cold. Recrystallization from 14 ml. of ethyl acetate gave 5.28 g. (52.2%) of the cyclic urethan, m.p. 79–80°. The analytical sample had m.p. 82–83°.

Anal. Calcd. for $C_4H_7O_2N$: C, 47.5; H, 6.9; N, 13.9. Found: C, 47.1; H, 6.9; N, 13.6, 13.5.

Since this synthesis was accomplished, Dyer and Scott have reported the preparation of this urethan by reaction of ethylene carbonate with 3-aminopropanol.⁹

An attempt to prepare the 7-ring urethan from 4-aminobutanol by the above procedure gave only low polymer.

3,3,6-Trimethyl-2-dioxanone.—Propylene oxide (58.1 g., 1.0 mole), methyl α -hydroxyisobutyrate (295 g., 2.5 moles) and 0.4 g. of sodium were heated in a rocker bomb at 130–135° for 15 hours. A 34% conversion to a liquid, b.p. 91–92° (15 mm.), n_D^{25} 1.4298, was obtained. This liquid, 30 g., was saponified with aqueous sodium hydroxide, acidified and extracted with ether. The 22 g. of ether extractables was distilled at atmospheric pressure to give 13.4 g. of material, b.p. 205–208°, n_D^{25} 1.4316. Redistillation gave a distillate (b.p. 100–104° (20 mm.), n_D^{25} 1.4330) which solidified on standing. It was recrystallized from petroleum ether, m.p. 41–42°.

Anal. Calcd. for $C_7H_{12}O_3$: C, 58.3; H, 8.3. Found: C, 57.8; H, 8.3.

N-Methylethyleneurea.—A mixture of 57.6 g. of ethyleneurea and 128.3 g. of methyl tosylate was heated to 100°. An exothermic reaction occurred, raising the temperature to 180°. The mixture was allowed to cool and was diluted with a solution of 16.0 g. of sodium hydride in 200 ml. of

absolute ethyl alcohol. The precipitated sodium tosylate was filtered. Distillation of the filtrate gave 44.2 g. of liquid, b.p. 100–190° (13 mm.). It formed a semi-solid mass on standing. Ether, 100 ml., was added and the crystals were filtered to give 12.1 g. of N-methylethyleneurea, m.p. 68° (hygroscopic).

Anal. Calcd. for $C_4H_9ON_2$: N, 28.0. Found: N, 28.2.

Neopentylene carbonate was prepared *via* depolymerization of low polymer. The latter was obtained by heating equimolar portions of neopentylene glycol with diethyl carbonate, catalyzed by a small piece of sodium, gradually to 210° and distilling ethyl alcohol as formed. Reaction was completed by heating at 220° under vacuum for an additional hour. The sticky polymer was depolymerized in 75% yield by the method of Spanagel and Carothers.¹⁰ After recrystallization from ether the monomer melted at 110°.

Anal. Calcd. for $C_5H_{10}O_3$: C, 55.4; H, 7.7; mol. wt., 130. Found: C, 55.4; H, 7.5; mol. wt., 147, 151 in boiling benzene.

Tetramethylethylene carbonate was prepared from pinacol and diethyl carbonate with a little sodium catalyst, m.p. 181–182° from ethyl alcohol.

Anal. Calcd. for $C_7H_{12}O_3$: C, 58.3; H, 8.4. Found: C, 58.3, 58.6; H, 8.8, 8.8.

N-Acetyleneurea was prepared by refluxing ethyleneurea with acetic anhydride, m.p. 171.5–173.0°, from acetonitrile.

Anal. Calcd. for $C_5H_8O_2N_2$: C, 46.9; H, 6.3; N, 21.9. Found: C, 46.9; H, 6.1; N, 21.5.

6,6-Dimethyl- δ -valerolactone was prepared by lactonization of 5-methyl-5-hexenoic acid.¹¹

The following compounds were used as received from the Eastman Kodak Co.: coumarin, benzoxazolone, benzthiazolone, phthalide, N-*n*-amylsuccinimide. The Aldrich Chemical Co. supplied the lactone of *trans*-2-hydroxycyclohexaneacetic acid.

Polymerizations.—The monomer, 2–4 g., was heated with catalyst, 0.1 g., in a long glass tube under a nitrogen atmosphere. Heating was provided by refluxing liquid-vapor baths. Heating was continued until the molten monomer had become very viscous or had solidified. The tube was cooled and broken open. The polymer was freed of monomer by extraction with appropriate solvents.

(10) E. W. Spanagel and W. H. Carothers, *ibid.*, **57**, 929 (1935).

(11) C. J. Albisetti, N. G. Fisher, M. J. Hogsed and R. M. Joyce, *ibid.*, **78**, 2637 (1956).

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(9) E. Dyer and H. Scott, *THIS JOURNAL*, **79**, 672 (1957).

[CONTRIBUTION FROM THE PIONEERING RESEARCH DIVISION, TEXTILE FIBERS DEPARTMENT, E. I. DU PONT DE NEMOURS AND CO., INC.]

Polymerization and Ring Strain in Bridged Bicyclic Compounds

BY H. K. HALL, JR.

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The polymerizabilities of a variety of atom-bridged bicyclic lactams, lactones, carbonates, ureas, urethans, imides and anhydrides were found to be determined by the type of ring structure, as indicated by conformational analysis. Compounds belonging to the bicyclo[2:2:2]octane and bicyclo[3:2:2]nonane series, in which the cyclohexane ring occurs in the boat form, underwent polymerization readily. Monomers of the bicyclo[3:2:1]octane group underwent polymerization with varying facility. Compounds of the bicyclo[3:3:1]nonane series, wherein two stable chair forms of cyclohexane are fused together, were not polymerizable.

Introduction.—Earlier papers of this series dealt with the polymerizability of monocyclic and bond-bridged bicyclic compounds.^{1,2} The present article extends this study to atom-bridged bicyclic compounds.

Several examples of the polymerization of such compounds have been recorded. The lactams 2-azabicyclo[3:2:1]octan-3-one I³ and 2-azabicyclo[3:2:2]nonan-3-one II⁴ when heated with water

(1) H. K. Hall, Jr., *THIS JOURNAL*, **80**, 6404 (1958).

(2) H. K. Hall, Jr., and A. K. Schneider, *ibid.*, **81**, 6409 (1959).

(3) Swiss Patent 270,546 (1951), to Inventa A. G. Lucerne; *cf.* A. J. Hall, *Fibers*, **18**, 402 (1957).

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