Polymer Bulletin 3, 233–239 (1980)

Polymer Bulletin

Anti-Bredt Monomers
5. Synthesis and Polymerization of 1-Aza-6-Oxabicyclo [3.2.1] Octan-7-One

H. K. Hall, Jr. and Ali El-Shekeil

Department of Chemistry, College of Liberal Arts, University of Arizona,
Tucson, Arizona 85721, USA

Summary

1-Aza-6-oxabicyclo[3.2.1]octan-7-one **3** polymerized in bulk to polyurethane at 112-131°C with opening of the 5-membered urethane ring. Organometallic, cationic, anionic and organophosphoric initiators polymerized the strained bicyclic urethane to the polyurethane. In solution the monomer was shown to polymerize slowly under the influence of phosphoric acid. The driving force for the polymerization may be the relief of strain energy in the monomer caused by a boat conformation of the 6-membered ring.

Introduction

According to Bredt's rule (BREDT et al. 1924, LUKES 1939), bicyclic [2.2.2] lactams with a bridgehead nitrogen atom should be very unstable because of the lack of N-C=O resonance, and because of the occurrence of a two-boat conformation (HALL 1958). For a [3.3.1] N-bridgehead lactam (HALL and SHAW 1980) and a [3.3.1] N-bridgehead urethane (HALL and EL-SHEKEIL 1980), the molecules were transformed from their usual two-chair conformations into less stable boat-chair conformations in order to permit N-CO overlap to occur (WISEMAN 1970). In the present case we have studied the polymerization of the next smaller bicyclic urethane, 1-aza-6-oxabicyclo[3.2.1]octan-7-one **3**.

0170-0839/80/0003/0233/$01.40

Instrumentation

NMR spectra were obtained using a Varian T-60 instrument. Infrared spectra were determined on a Perkin-Elmer 337 grating infrared spectrophotometer. Mass spectra were determined on a Hewlett-Packard 5930 A quadrupole mass spectrometer. Elemental analyses were performed by Chemalytics, Inc., Tempe, Arizona or by the University Analytical Center, Department of Chemistry, University of Arizona, Tucson. The number-average molecular weight of polymers were determined on dichloroethane solutions at 37°C using Hewlett-Packard Vapor Pressure Osmometer, Model 302B. Melting points were determined in °C in a Thomas-Hoover melting point apparatus and are uncorrected.

Experimental

3-Hydroxypiperidine (3.6 g, 35.6 mmole) was dissolved in dry dichloromethane with an equimolar amount of triethylamine (5 ml) and cooled to -60° in a Dry Ice-isopropyl alcohol bath. Phosgene was condensed in a graduated trap at -60° and transferred to the reaction vessel with the aid of 20 ml cool dichloromethane. After 15 min. at room temperature, the solvent was removed on a rotary evaporator at 25° and the 3-hydroxypiperidinocarbamoyl chloride was extracted in 180 ml dry toluene (yield 87.3% as triethylamine hydrochloride, 4.28 g). To the toluene solution, 20 ml (0.142 mol) triethylamine was added and additional triethylamine hydrochloride started precipitating out immediately. The flask was refluxed for 1 hr at 90° (100° oil bath), then white triethylamine hydrochloride was filtered, toluene removed on a rotary evaporator at 50°, and the brown residue was distilled in kugelrohr at 98° (0.01 mm) giving 1.72 g of the [3.2.1]bicyclic urethane. The residue in the distillation flask was dissolved in dichloromethane and added dropwise to 400 ml of ethyl ether in a 500 ml beaker. Polymer precipitated out (1.40 g, 31% yield). The ether was evaporated to give 1.05 g of the monomer. Total overall yield of monomer 61.3%, mp 112-113°. To eliminate the formation of polymer, the crude monomer, in another experiment, was precipitated from ether at -50°, ether decanted and the monomer was sublimed at 0.001 mm. and 25°-45°C to give 73% overall yield.

nmr ($CDCl_3$) δ: 4.80 (t(m?), 1H); 3.30 (m, 4H; 1.95 (m, 4H)

ir (KBr): C=O stretch, 1770 cm^{-1}; C-H stretch, 2940 cm^{-1} and 2860 cm^{-1} (broad). Overtone of C=O 3540 cm^{-1}. (SILVERSTEIN, BASSLER, MORRILL 1974)

Mass Spectra (5 eV): 127 m/e; calc'd: 127

Anal. Calc'd for $C_6H_9NO_2$:	C 56.69,	H 7.09,	N 11.02
Found:	56.37	7.20	10.92

Polymerizations

The polymerizations were done in dry vials charged with monomer and initiator. The reaction vessel was subjected to heat in a thermostat-connected oil bath for 18-24 hrs. The polymers were dissolved in dichloromethane and precipitated from ethyl ether, then dried at 60°.

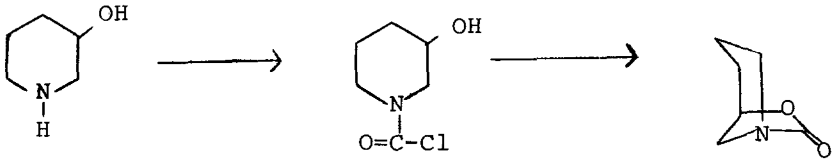
nmr ($CDCl_3$) δ: 3.63 (m, 1H); 3.84 (m, 4H); 1.7 (m, 4H).

ir (KBr): C=O stretch 1680 cm^{-1}, C-H stretch 2860 and 2945 cm^{-1}.

Anal. Calc'd for $C_6H_9NO_2$:	C 56.7,	H 7.1,	N 11.0
Found:	56.7	7.1	11.0

Results

By treating 3-hydroxypiperidine with phosgene and triethylamine in dichloromethane followed by four equivalents of triethylamine in toluene, the compound 1-aza-6-oxabicyclo[3.2.1]-octan-7-one was synthesized in two easy steps. The carbamoyl chloride intermediate 2



1 2 3

was not easy to purify and hence was prepared in situ and used without purification. Monomer 3 can be sufficiently purified by vacuum distillation at room temperature for polymerization studies. It is unstable at room temperature and tends to polymerize slowly in the presence of air. Thus 3 was stored at -50°C.

Polymerization of 3 was attempted in solution first (TABLE I). It seemed fairly stable. It resisted

TABLE I. Polymerization of 1-Aza-6-oxabicyclo[3.2.1] octane-7-one in Solution

Monomer (mg)	Initiator	Solvent (ml)	Time, hr.	Temp. °C	Result
60	KOtBu (3 mg)	DMSO-d_6 (0.5)	24	105°	NR
60	HOTs H_2O (4 mg)	DMSO-d_6 (0.5)	24	105°	NR
60	85% H_3PO_4 (6 mg)	DMSO-d_6 (0.5)	24	105°	polymer
103	KOtBu (2 mg)	$(CH_2)_2Cl_2$ (0.2)	18	65°	NR
103	KOtBu (2 mg)	$(CH_2)_2Cl_2$ (0.2)	23	124°	polymer/ monomer (∿1:1)
91	85% H_3PO_4 (3 mg)	$(CH_2)_2Cl_2$ (0.2)	18	65°	NR
91	85% H_3PO_4 (3 mg)	$(CH_2)_2Cl_2$ (0.2)	23	124°	polymer

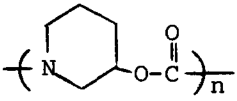
anionic (KOtBu) and cationic ($HOTs{\cdot}H_2O$) initiators in DMSO-d_6, but it polymerized slowly under the influence of KOtBu in dichloroethane and about 1:1 monomer to polymer ratio was obtained after 23 hrs at 124°. Phosphoric acid polymerized it in DMSO-d_6 and dichloroethane.

When the monomer was polymerized in bulk, it showed high reactivity (TABLE II). The structure of the polymer is **4** and it was obtained using anionic, cationic, organometallic, organophosphinic and organophosphonic initiators. Polymer **4** was soluble in dichloromethane and dichloroethane but insoluble in ether and toluene. White-to milky brittle films can be made. The white powdered **4** are electrostatic when dry and melt at 165-174°. The polymers showed the number average molecular weight from 1400 to 2600.

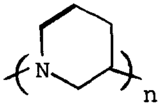
TABLE II. Polymerization of 1-Aza-6-oxabicyclo[3.2.1] octane-7-one in Bulk

Monomer (mg)	Initiator (mg)	Time, hr	Temp °C	Yield (%)	m.p.
200	Dibutyltinoxide (4.4 mg)	22	112°	165 mg (83%)	145-150
210	KOtBu (2 mg)	23	114°	200 mg (95%)	150-163
184	KOtBu (2 mg) + ϕNCO (trace)	23	114°	180 mg (98%)	148-165°
216	$HOTs{\cdot}H_2O$ (3 mg)	22	112°	196 mg (91%)	158-165°
166	Phenylphosphonic acid (2 mg)	18	131°	130 mg (78%)	165-174°
142	Phenylphosphinic acid (2 mg)	18	131°	95 mg (67%)	150-157

Polymer **5** might have formed by loss of CO_2 from the urethane monomer on heating (SONNERSKOG 1956 and JONES 1956), but it was not detected.



4



5

Discussion

The title compounds 1-aza-6-oxabicyclo[3.2.1] octan-7-one **3** polymerizes readily. This is readily ascribable to the inhibition of N-CO overlap in the chair monomer which forces the molecule into the boat form (WISEMAN 1970). Overlap is fully recovered in stainless chair-containing polymer **4**. The inhibition is greater in monomer **3** (fused 5- and 6- rings) than in the higher homolog 1-aza-3-oxabicyclo[3.3.1]nonan-2-one (two fused 6-rings) studied previously (HALL and EL-SHEKEIL 1980), and so higher reactivity is noted.

However, bicyclo[3.2.1]octane monomers consisting of a 5-membered ring fused to a chair cyclohexane in the 1,3 diaxial position also polymerize (HALL 1958, HALL 1960, SUMITOMO and HASHIMOTO 1971, SUMITOMO, HASHIMOTO, and ANDO 1973; (review) SUMITOMO and OKADA 1978). Ring-opening polymerization of the 5-membered ring permits the substituents to achieve the stabler 1,3-di-equatorial positions.

The correct explanation for the polymerizations observed depends on whether monomer **3** adopts the boat form suggested by Wiseman's rule or the chair form taken by other bicyclo[3.2.1]monomers not possessing the bridgehead N-CO structure. A crystal structure determination is currently in progress to answer this question.

Acknowledgements

The authors are deeply indebted to the University of Sanaa, Yemen, for scholarship to A. E. and National Institute of Health GM 18595 for support.

References

Paper 4 in this series: H. K. HALL, JR., and A. EL-SHEKEIL: Polymer Bulletin, submitted (1980)

J. BREDT, H. THOUET, and J. SCHMITZ: Ann., 437, 1 (1924)

J. I. JONES: Chemistry and Industry, 1454 (1956)

H. K. HALL, JR.: J. Am. Chem. Soc. 80, 6412 (1958)

H. K. HALL, JR.: J. Am. Chem. Soc., 82, 1209 (1960)

R. LUKES: Collect.Czech.Chem. Commun., 10, 148 (1939)

R. M. SILVERSTEIN, G. C. BASSLER and T. C. MORRILL: Spectroscopic Identification of Organic Compounds, 3rd. Ed., John Wiley and Sons, Inc., New York, 1974, p. 98.

S. SONNERSKOG: Acta Chem. Scand., 10, 467 (1956)

H. SUMITOMO, K. HASHIMOTO: Macromolecules 10, 1327 (1971)

H. SUMITOMO, K. HASHIMOTO, and M. ANDO: J. Polym. Sci., Polym. Lett. Ed., 11, 635 (1973)

H. SUMITOMO and M. OKADA: Adv. Polym. Sci., 28, 48 (1978)

J. R. WISEMAN: J. Amer. Chem. Soc., 92, 956 (1970)

Received and accepted September 18, 198o