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Anti-Bredt Monomers
4. Polymerization of 1-Aza-3-Oxabicyclo [3.3.1]Nonan-2-One

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

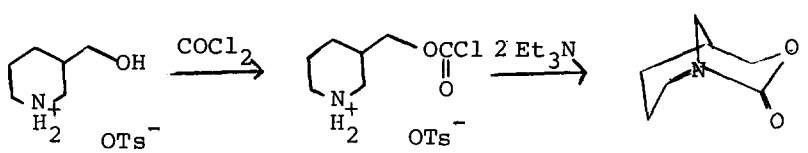
Department of Chemistry, College of Liberal Arts, University of Arizona, Tucson, Arizona 85721, USA

Summary:

1-Aza-3-oxabicyclo[3.3.1]nonan-2-one, an N-bridgehead bicyclic urethane, polymerized in bulk under the influence of dibutyltin oxide and p-toluenesulfonic acid. In solution the monomer polymerizes in the presence of phosphoric acid. This is only the second example of ring opening polymerization of a bicyclo-[3.3.1]nonane. The driving force in the present case is thought to be the relief of strain energy in the monomer conferred by its chair-boat conformation.

Introduction:

A characteristic feature of title compound 3 is the presence of the bridgehead nitrogen atom, which is a cause of instability since the N-CO resonance interaction is prohibited if the molecule exists in a two-chair form (BREDT, THOUET, and SCHMITZ 1924, LUKES 1939, WISEMAN 1970).



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Although the presence of the adjacent oxygen atom partially satisfies the demand of the carbonyl group for electrons, this compound is expected to polymerize to recover full N-CO resonance interaction as well as a strainless chair conformation.

Instrumentation:

NMR spectra were obtained using Varian T-60. 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. All the melting points were determined in °C in a Thomas-Hoover melting point apparatus and are uncorrected.

Experimental:

3-(Hydroxymethyl)piperidinium p-Toluenesulfonate Salt 1

3-Piperidinemethanol (bp 72°/0.05 mm, 20.7 mmole, 2.38g) was dissolved in 50 mL absolute ethyl alcohol (warm). An equimolar amount of p-toluenesulfonic acid momohydrate (3.93g) was added. When anhydrous ether was added, a white cloud appeared which condensed into an oil. This oil solidified by cooling at 10° for 3 days and white needle crystals appeared above it. This was filtered and recrystallized from an ethyl acetate ethanol mixture (1:1), mp 76-78°, 54% yield.

CHN analysis as calculated for $C_7H_{11}NO_2$:

Calc:	C 54.36	H 7.32	N 4.88	S 11.15
Found:	53.32	7.33	4.38	11.42

3-Chloroformyloxymethylpiperidinium p-Toluenesulfonate Salt 2

3-Piperidinemethanol p-toluenesulfonate salt (9.22 g, 30 mmole) was dissolved in 100 mL dry dichloromethane. The solution was poured into a 3 neck 500 mL Morton flask fitted with a condenser, a thermometer and the third neck for passing phosgene and nitrogen. The exit from the condenser was protected with a U-tube oil trap. The apparatus was dried with a Bunsen flame and cooled under a stream of nitrogen before pouring the solution. The system was magnetically stirred and kept at 0° using a Dry Ice-isopropyl alcohol bath. Phosgene (60.6 mmole, 6g, 6.3 mL) was condensed in a small graduated trap using a Dry Ice-isopropyl alcohol bath and passed into the solution by a stream of dry nitrogen (exiting to NaOH). The reactions was completed in 90 min. The chloroformyloxy salt prepared was rotevaporated to a brownish paste, which solidified under vacuum. The crude yield was 92%.

ir (neat): C=O stretch at 1780 cm^{-1}. N-H stretch at 3400 cm^{-1}. No OH absorption.

nmr ($CDCl_3$): Quartet at δ7.5 (4H), doublet δ4.2 (2H), multiplets δ3.8 to δ1.0 and singlet δ2.2 (14H).

Attempted recrystallization of this salt led to decomposition.

1-Aza-3-oxabicyclo[3.3.1]nonan-2-one 3

3-Chloroformyloxymethylpiperidine p-toluenesulfonate salt (2.3g, 6.26 mmole) was dissolved in 200 mL dry dichloromethane and added dropwise from a pressure equalized funnel to 12.52 mmole (1.75 mL) triethylamine (distilled from CaH_2) in 300 mL dichloromethane. The addition was over in 1 hr. The solvent was

rotevaporated to dryness. The residue was transferred to a soxhlet thimble and extracted with ether for 8 hr, filtered, and rotevaporated leaving 0.74 g of white crystals, which melted at 144-146°; yield, 84%. NMR ($CDCl_3$) and infrared spectra were completely identical with authentic sample prepared by another method (HALL and EL-SHEKIEL, 1980).

The urethane can be distilled in a kugelrohr and sublimed (mp 146-147°), yield 28 %.

ir: C=O at 1710 cm^{-1}, CH at 2935 and 2860 cm^{-1}
nmr: ($CDCl_3$) doublet of doublets δ4.8 (1H), doublet δ4.2 (1H), multiplets δ4.1 to δ2.7 (4H), multiplet δ2.2 (1H), multiplet δ1.7 (4H).
M.S.: Calc'd for $C_7H_{11}NO_2$ 141.2. Found: 141.2
CHN: Calc'd C 59.57 H 7.80 N 9.93
Found 59.35 7.76 10.00

Polymerizations:

The polymerizations were done in dry vials charged with monomer and initiator. The reactions vessel was heated in a thermostated oil bath. The polymers were dissolved in dichloromethane and precipitated from ethyl ether, then dried at 60°.

ir: C=O at 1680 cm^{-1}
nmr: Multiplets δ4.6 - 1.2.
CHN: Calc'd C 59.6 H 7.8 N 9.9
Found 58.9 7.6 9.4

Results:

1-Aza-3-oxabicyclo[3.3.1]nonan-2-one $\underset{\sim}{3}$ was synthesized by the cyclization of 3-chloroformyloxymethylpiperidine hydrotosylate salt $\underset{\sim}{2}$ with two equivalents of triethylamine in dry dichloromethane at

room temperature. The chloroformyloxy salt $\underset{\sim}{2}$ was not easy to purify and hence was prepared in situ and used without purification. The monomer $\underset{\sim}{3}$ can be sufficiently purified, by vacuum molecular distillation or sublimation, for polymerization studies.

The polymerization of $\underset{\sim}{3}$ was attempted in solution (TABLE I). The monomer was stable to water, cationic ($HOTs \cdot H_2O$) and anionic (KOtBu) initiators but phosphoric acid polymerized it after 24 hr. at 105° in DMSo-d_6.

TABLE I

Polymerization of 1-Aza-3-oxabicyclo[3.3.1]nonan-2-one in solution[a,b]

Initiator (mg)	Solvent (0.5mL)	Time, hr	Temp°C	Result
H_2O (250)	$CDCl_3$	16	84	NR
KOtBu (3)	DMSO-d_6	16	84	NR
$HOTs \cdot H_2O$ (5)	$CDCl_3$	16	84	NR
H_3PO_4 (∿1mg)	DMSO-d_6	27	105	Polymer

a: 60 mg of monomer used in each case.

b: Polymerization monitored by running the reaction in NMR tube and comparing spectra before and after the reaction.

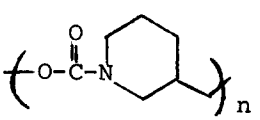
Attention was directed towards polymerization of $\underset{\sim}{3}$ in bulk at its melting point temperatures or higher (TABLE II). It showed low reactivity and only dibutyltinoxide and p-toluenesulfonic acid polymerized it. In case of dibutyltin oxide the polymer obtained showed $\bar{M}n$ of 2300, mp 181-184°, soluble in dichloromethane. p-Toluenesulfonic acid polymerized $\underset{\sim}{3}$ to a lower polymer ($\bar{M}n$ = 1200). Potassium t-butoxide, potassium t-butoxide acid and phenylphosphinic acid gave only a trace of polymer.

TABLE II

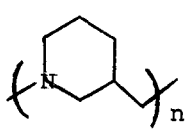
Polymerization of 1-Aza-3-oxabicyclo[3.3.1]nonan-2-one in Bulk

mg Monomer	Initiator (mg)	Time, hr	Temp° C	Yield mg(%)	mp	M.W.
106	Dibutyltin-oxide (∿4)	19	150	54 (51%)	181-184	2300
105	KOtBu (∿3)	19	150	trace	--	--
122	KOtBu (∿3) + ØNCO (trace)	19	150	trace	--	--
111	$HOTs \cdot H_2O$ (∿3)	18	190	12 (11%)	181-190	1200
87	Phenylphos-phonic acid (∿2)	18	190	trace	--	--
64	Phenylphos-phonic acid (∿2)	18	190	trace	--	--

The polymer obtained had structure $\underset{\sim}{4}$ by IR, NMR and elemental analysis. Although structure $\underset{\sim}{5}$ might

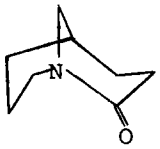


$\underset{\sim}{4}$



$\underset{\sim}{5}$

have formed by loss of carbon dioxide from the bicyclic urethane monomer on heating (SONNERSKOG 1956 and JONES 1956) we were unable to detect its presence.



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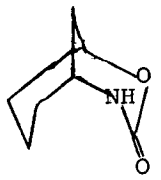

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Discussion:

Bicyclic urethane 3 is only the second bicyclo-[3.3.1]nonane derivative found to undergo ring-opening polymerization. The only previous polymerizable monomer of this group is the homomorphic lactam 1-azabicyclo[3.3.1]nonan-2-one 6 (HALL and SHAW 1980). Other bicyclo[3.3.1]nonanes, lacking the bridgehead N-CO structure did not polymerize (HALL 1958a, 1958b, 1960; HALL and SCHNEIDER 1958). In particular the isomeric urethane 2-aza-4-oxabicyclo[3.3.1]nonan-2-one 7 did not do so.

Bicyclo[3.3.1]nonane derivatives usually adopt a two-chair conformation (PETERS 1979). The nmr spectra of N-bridgehead monomers 3 and 6 suggests that they adopt boat-chair conformations in order to permit substantial N-CO overlap (HALL and WISEMAN 1970, SHAW 1980, HALL and EL-SHEKEIL 1980). However, the boat conformations are unstable and renders these monomers polymerizable. The polymer, possessing only a single chair conformation and full N-CO overlap, is strainless and is stable at equilibrium.

Acknowledgements:

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