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Anti-Bredt Molecules

6. Synthesis and Polymerization of 1,3-Diazabicyclo [3.3.1]Nonan-2-One

H. K. Hall, Jr.*, Oluchukwu E. Ekechukwu, A. Deutschmann, Jr.[1] and C. Rose

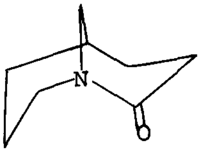
Department of Chemistry and [1]Department of Nutrition and Food Sciences,
University of Arizona, Tucson, Arizona 85721, USA

SUMMARY

An "anti-Bredt" bicyclic urea, 1,3-diazabicyclo-[3.3.1]nonan-2-one, was synthesized. At 125° this urea polymerized thermally and at 98° it rapidly polymerized under the influence of phosphoric acid. Two isomeric ureas, lacking the anti-Bredt feature, did not polymerize under similar conditions.

INTRODUCTION

Inhibition of the N-CO resonance in N-bridgehead bicyclic lactams of the [2.2.2]octane series leads to high reactivity and polymerizability (PRACEJUS, 1965). We have found polymerizability in two N-bridgehead bicyclo[3.3.1]nonane derivatives, lactam 1 (HALL, SHAW, and DEUTSCHMANN, 1980) and urethane 2 (HALL and EL-SHEKEIL, 1980).



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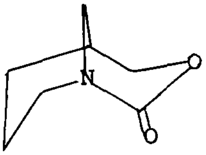

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Isomeric bicyclo[3.3.1]nonane urethanes and lactams lacking this "anti-Bredt" feature did not polymerize. In this work we examine the corresponding bicyclic urea.

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* To whom inquiries should be addressed

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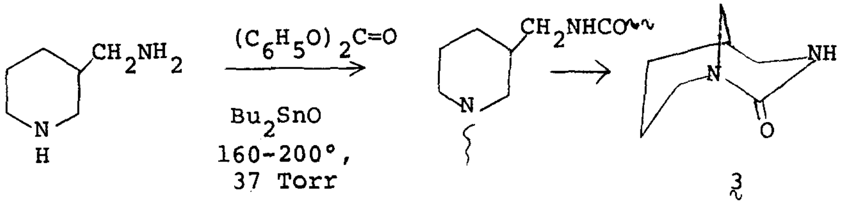
Synthesis -

Reaction of 3-(aminomethyl)-piperidine with diphenyl carbonate gave pre-polyurea. Depolymerization under high vacuum and high temperature gave a mixture which on HPLC gave a 26% yield of 3. To confirm the



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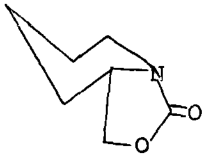
structure, reaction of phosgene with 3-aminomethylpiperidine in ether at 25° gave a N-carbamyl chloride hydrochloride, treatment of which with triethylamine gave urea 3 in 5% yield. The two routes gave identical product.

2-(Aminomethyl)-piperidine on similar treatments gave the isomeric bond-bridged bicyclic urea, 1,3-diazabicyclo[4.3.0]nonan-2-one 4 in 50% yield directly. No polymer was noted.



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Both ureas were fully characterized by IR, NMR, MS, and microanalysis.

Chemical Reactivity -

The ureas did not react significantly with D_2O at 70° or with D_2O/KOH at 70° in 2 hours. However, introduction of HCl into a D_2O solution of 3 at 28° gave immediate hydrolysis.

Polymerization -

Urea 3 polymerized thermally to polyurea with a half-life of ∿30 minutes at 125°. At 95° negligible thermal polymerization was noted in 2 hours. Urea 4 did not polymerize under this or any other conditions tried.

Results of bulk polymerization are given in Table I. We conclude that marked catalysis occurs with phosphoric acid, and higher inherent viscosities and yields were found with the other putative catalysts.

Polyurea -

The polyurea from 3 melted ∿210°, and short filaments could be drawn from the melt. It was insoluble in common organic solvents including dimethylformamide but dissolved in hexafluoroisopropanol.

DISCUSSION

Conformation and Strain -

The polymerization of 3 is somewhat surprising. We had expected that overlap of the C=O group with the nonbridgehead N might be extensive enough that the lack of overlap with the bridgehead N might not be significant. This is not the case. The monomer polymerizes to recover the full urea resonance involving both nitrogens.

In order to obtain as much overlap of both N's in the monomer, the molecule is expected to adopt a chair-boat conformation (HALL, SHAW, and DEUTSCHMANN, 1980). Evidence for this conformation is found in the nmr spectrum, wherein a downfield absorption for 1 H is ascribed to the equatorial H at C_8 which lies in the cone of the C=O group. Isomer 4, as well as a second isomer 5, (2,4-diazabicyclo[3.3.1]nonan-3-one, (HALL,

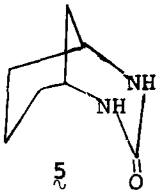

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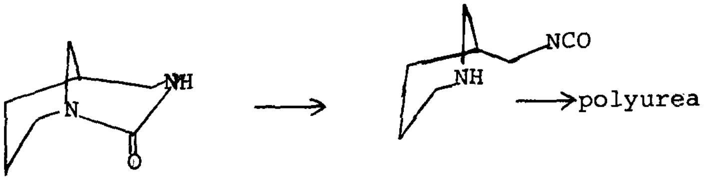
Table I. Polymerization of 1,3-diazabicyclo[3.3.1]nonan-2-one.

Weight of Urea (mg)	Catalyst	Polymerization temperature °C	Heating time (hr)	Weight and yield of polymer (mg)	m.p. of polymer, °C	Inherent viscosity 1%, HFIPA
202	none	120	6	100(55%)	200-210	0.64
204	$PhPO_3H_2$	120	6	150(74%)	200-210	0.81
202	Bu_2SnO	120	6	120(60%)	201-212	0.89
227	tBuOK	120	6	170(75%)	>220	1.23
202	none	95	24	none	-	-
204	H_3PO_4	98	2	110(54%)	>200	0.13

1958) can have full overlap of both nitrogens in the favored two-chair conformation. Therefore, they are not strained and do not polymerize.

Mechanisms -

Thermal polymerization of 3 probably proceeds by thermal dissociation to an aminoisocyanate which then undergoes polyrecombination (HALL and SCHNEIDER, 1958).



The mechanism for phosphoric acid initiation is obscure but it has long been known as a potent catalyst (HALL, 1958).

EXPERIMENTAL SECTION

Instrumentation -

Unless otherwise stated all melting points were uncorrected and were determined in a Thomas-Hoover capillary melting point apparatus, melting points, boiling points and reaction temperatures are recorded in degrees Celsius (°C). Nuclear Magnetic Resonance (NMR, 60MHz) spectra were determined on a Varian Model T-60 Spectrometer, NMR peak positions (chemical shifts) were expressed in parts per million (δ) downfield. Tetramethylsilane (TMS) was an internal standard. Mass spectra were recorded on a Hewlett-Packard 5930A quadrupole mass spectrometer of the University of Arizona Analytical Center. High Pressure Liquid Chromatography (HPLC) was accomplished using Altex Inc. Units. The HPLC was equipped with Spectra-Physics (SP 8200) 254 nm UV detector, Linear recorder and Altex pump. The column was 25mmx1m packed with Woelm dry column chromatography silica gel (activity III/30). Infrared (IR) spectra were obtained with a Perkin Elmer 710A grating infrared spectrophotometer. Inherent viscosities were determined with an Ostwald-Fenske viscometer. All hydrogenations were done at the University of Arizona High Pressure Laboratory equipped with various reactor sizes (Magna-drive) autoclaves. Some of the combustion analyses were performed by Chemalytics, Inc., Tempe, Arizona. The others were done by the University of Arizona Analytical Center.

Synthesis of 1,3-diazabicyclo[3.3.1]nonan-2-one, **3**. 3-aminomethylpiperidine (6.0 g, 52.5 mmole), (FREIFELDER and STONE, 1961), dibutyl tin oxide(200 mg)and diphenyl carbonate (12.7 g, 59.3 mmole) were intimately mixed in a 100 ml round-bottom flask at ambient temperature.They reacted exothermically. The temperature was raised with a heat gun till the mixture became homogeneous.The mixture was distilled in an Aldrich rocking Kugelrohr at 150-160° (37 Torr.) When nearly 2 equivalents of phenol (9.32 g, 99 mmole; theoretical 11.14 g,118.4 mmole)were collected in the second bulb,the batch was cooled to 60°, another 200 mg of dibutyl tin oxide was added, and a fresh receiver was attached to receive the crude product. The temperature of the brittle glassy material in the flask was raised gradually to 215-230° (0.05 Torr.) as the flask and the bulbs were rocked. The depolymerized viscous, faint yellow, heterogeneous soft solid distillate (5.0 g) was chromatographed on an HPLC over silica gel, eluting phenol first with 100% CH_2Cl_2. The solvent was then changed to 100% THF, and the title compound was eluted. Rotoevaporation followed by recrystallization from methyl acetate afforded 2.0 g of **3**. Yield 27%. The crystals softened and appeared to swell at 98-100°, transformed to amorphous material which changed viscosity and flowed as globules at 133-135°.

Analysis: Calculated for $C_7H_{12}N_2O$: C, 59.95; H, 8.65; N, 19.98

Found: C, 59.90; H, 8.80;
N, 20.00

IR(KBr): 3300 (m), 3200(s), 3090, 2925(s), 1660(s), 1480(s), 1410(s), 1330(s), 1280(s), 1180(s), 1020(s), 800(s) cm^{-1}

NMR($CDCl_3$): δ 6.3 (1H, Singlet); 4.0-2.5(6H, multiplets) 2.0-1.2 (5H, multiplets)

MS: m/e 140 (M^+, base), base-57; base-70

Synthesis of 1,8-diazabicyclo[4.3.0]nonan-9-one, 4. - A mixture of 2-aminomethylpiperidine (3.03 g, 26.5 mmole), diphenyl carbonate (6.35 g, 29.64 mmole) and dibutyl tin oxide (400 mg) was heated with a heat gun till a wine-red solution resulted. Two equivalents of phenol were removed by distillation at 160-170° (37 Torr.) The residue was short-path distilled at 190°(2.5 Torr.) The distillate, 2.09 g, was taken up in dry 50/50 ether/THF mixture and chilled at -50° for 2 days. The product was collected by filtration. When the filtrate was concentrated and chilled at -50° for 2 days, a second crop of the product was obtained. The combined product was sublimed at 50-65° (oil bath temperature) and 0.05 Torr. Yield: 1.28 g (35%), mp 69-70°.

IR: 3275(s), 2945(s), 2850(s), 1680 and 1660(s), 1490(s), 1460, 1440, 1280(s), 1180(s), 1110(s), 1060, 950, 750 cm^{-1}

NMR:($CDCl_3$): δ5.2 (1H, singlet); 4.0-2.4 (5H, multiplets); 2.0-1.0 (6H multiplets)

MS: $M^{\cdot +}$ 140

Analysis: Calculated for $C_7H_{12}N_2O$: C, 59.95; H, 8.65;
N, 19.98.
Found: C, 59.80; H, 8.40;
N, 20.00.

Polymerization - The urea **5** (about 10 mg) was sealed in melting point capillary tubes. Duplicates were heated in thermostated oil baths at various times and temperatures. Their IR spectra were taken in KBr pellets and compared against the IR spectrum of a reference unheated sample. Shifts of the carbonyl absorption from 1660 cm^{-1} to 1620 cm^{-1} and changes in the finger print region of the IR spectra from sharp to featureless indicated polymerization.

In initiated polymerizations, a mixture of about 200 mg of urea $\underset{\sim}{3}$ and trace amounts of initiator was heated at 120-125° for 6 hours in an evacuated sealed vial. The hard glassy transparent polymer was first stirred in 1,2-dichloroethane, then in dimethyl formamide (DMF), tetrahydrofuran (THF) and lastly in glyme, none of which dissolved the polymer, to extract any unreacted monomer. The tough polymer was dried and the melting point taken. The polymer was completely soluble in 1,1,1,3,3,3-hexafluoro-2-propanol in which viscosity measurements were made.

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