Anti-Bredt Bridgehead Nitrogen Compounds in Ring-Opening Polymerization

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Contents

H. K. Hall, Jr., was born in New York City in 1924. He received his undergraduate training at Brooklyn Polytech, a Master's degree at Penn State, and a Ph.D. degree from the University of Illinois in 1949. Postdoctoral work followed, with Prof. P. J. Flory at Cornell and with Profs. S. Winstein and W. G. Young at U.C.L.A. He put in a 17-year period with Du Pont in Wilmington, 13 in the Pioneering Research Laboratory and 4 at the Central Research Department. In 1969, Hall moved to the University of Arizona and became the head of the Chemistry Department. In 1973, he thankfully relinquished that post to return to research and teaching. Hall's research interests have included the mechanisms of reactions of acyl chlorides and of amines, the synthesis and ring-opening polymerization of strained bicyclic molecules, and the mechanisms of reaction of donor with acceptor olefins.

Ali El-Shekeil was born in Yemen in 1948. He received his bachelor's degree from Baghdad University, (Iraq) in 1974 and his Ph.D. from the University of Arizona in 1980, where he undertook a program of research under the direction of Dr. Henry Hall, Jr., on anti-Bredt nitrogen-bridgehead bicyclic urethanes. He is now a staff member in the Chemistry Department, University of Sana's (Yemen), and Vice-dean of the Faculty of Science. His research interests are the synthesis and polymerization of anti-Bredt nitrogen-bridgehead bicyclic compounds.

I. Bredt's Rule

A. Bicyclic Bridgehead Olefins and Imines

Bredt's rule expressed the idea that carbon–carbon double bonds at the bridgeheads of certain bicyclic systems would be incapable of existence. The reason for this prohibition is that in such olefins the p orbitals, whose overlap comprises the π bond in normal olefins, are held perpendicular to each other. The exact limits of applicability of this rule have been probed by many resourceful investigators. At present, it appears that the following three bicyclic olefins are at the limits of isolability: bicyclo[3.3.1]non-1-ene (**1**)[2-4] bicyclo[4.2.1]non-1-ene (**2**),[4,5] and bicyclo[4.2.1]non-8-ene (**3**):[5]

1 2 3

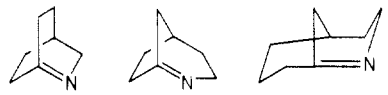
Olefins detected by trapping but not isolated include the following among others:

0009-2665/83/0783-0549$06.50/0

4[6] 5[7,8] 6[9] 7[9]

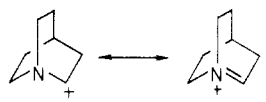
Wiseman and Chong[9] stated that "ordinarily a bridgehead double bond will be more stable when it is *trans* in the larger of the two rings in which it is endocyclic." This insight enabled them, for example, to assign the chair–boat structure rather than the two-chair structure to bicyclo[3.3.1]non-1-ene (1).

Imines in which the carbon–nitrogen double bond possesses similar geometry to its olefinic analogue, are also subject to Bredt's rule limitations. Anti-Bredt imines reported to date, either isolated or as intermediates, include



8[10,11] 9[10,11] 10[12]

Although immonium ions should be similarly restricted, Grob and Sieber[13] report that the carbenium ion 11 is significantly stabilized by the adjacent bridgehead nitrogen:

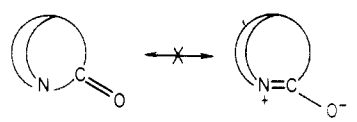


11

Excellent reviews of these topics have been published by Koebrich,[11] Buchanan,[14] Greenberg and Lieberman,[15] and Szeimies.[16]

B. Bicyclic Compounds Possessing Bridgehead N—C=O Groups

Lukes[17] pointed out in 1939 that similar restrictions should apply to N-bridgehead compounds possessing adjacent carbonyl groups because resonance stabilization of the N—C=O moiety would create a (forbidden) bridgehead double bond.



The applicability of this statement will be investigated. The strain in the N-bridgehead anti-Bredt bicyclic compounds will also be discussed in relation to their instability and their potential as monomers in ring-opening polymerization.

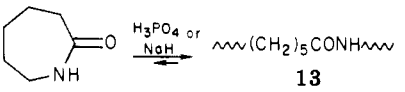
II. Ring-Opening Polymerization

Ring-opening polymerization consists of the formation of linear high polymers by the linking together of rings. As will be seen, it is a very sensitive technique for the detection of strain in organic molecules.

Early work in this area, as well as the accomplishments of himself and his colleagues, was reviewed by W. H. Carothers.[19] Subsequently, Dainton and Ivin[20] and Small[21] covered the area. Two books on this topic[22,23] have been published, and another, edited by Ivin and Saegusa, is in press.[24]

A. Monocyclic Monomers

Many monocyclic lactams, lactones, ethers, etc., undergo reversible ring-opening polymerization when exposed to ionic initiators. For example, caprolactam (12) polymerizes when heated with either sodium hydride or phosphoric acid to form the linear poly-6-caproamide (13):

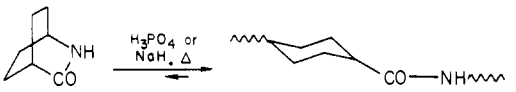


12 13

The thermodynamic driving force for ring-opening polymerization is the release of strain. This can originate from angle strain in three- or four-membered rings, H–H eclipsing in five- to seven-membered rings, and transannular hydrogen crowding in eight- to twelve-membered rings. Substituents on a ring are always unfavorable, regardless of their nature because through conformational effects they favor cyclization.[18]

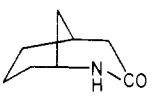
B. Atom-Bridged Bicyclic Monomers

Similarly, atom-bridged bicyclic monomers were shown by Hall[25] to undergo ring-opening polymerization. For example, 2-azabicyclo[2.2.2]octan-3-one (14) polymerized when heated with sodium hydride or phosphoric acid to a linear polyamide:



14 15

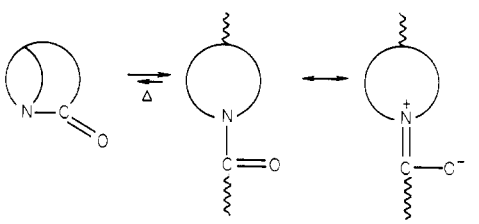
The thermodynamic driving force was the relief of strain in the boat cyclohexane ring upon conversion to the chair form in the polymer chain. Under the same conditions 2-azabicyclo[3.3.1]nonan-3-one (16), existing



16

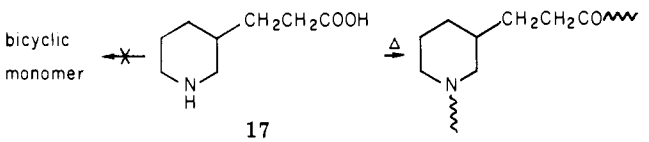
in the stable two-chair form, was recovered unchanged. Here the relatively strainless two-chair structure provided negligible driving force for polymerizations. Other bicyclo[3.3.1]nonane ureas and urethanes which did not possess bridgehead nitrogen were also nonpolymerizable.[25]

An anti-Bredt bicyclic lactam, if it could be synthesized, would possess an additional driving force for polymerization compared to the bicyclic bridged lactams, because the N—C=O resonance energy would be recovered in the polymer



In keeping with this idea, heating 3-piperidinepropionic acid (17) at atmospheric pressure gave only polyamide.[26] The Bredt rule instability of the putative lactam out-

weighs the customary stability of a bicyclo[3.3.1]nonane derivative

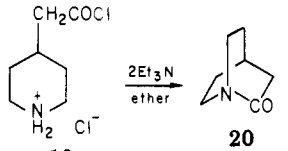


17 18

III. Synthesis of N-Bridgehead N—C=O Compounds

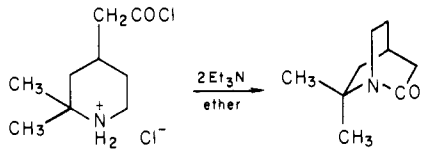
A. Lactams

2.2.2 System. In 1957, Yakhontov and Rubsitov reported the synthesis of the parent 1-azabicyclo[2.2.2]-octan-2-one (**20**) from the ammonium salt–acid chloride **19**.[27,28]



19 20

Another step forward was the synthesis of 6,6-dimethyl-2-quinuclidone (**22**) and 6,6,7-trimethyl-2-quinuclidone (**24**) by Pracejus,[29-31] who used the same reaction.



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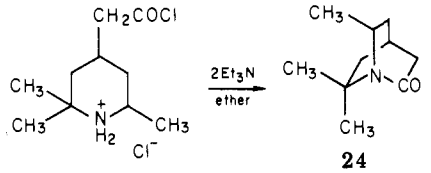
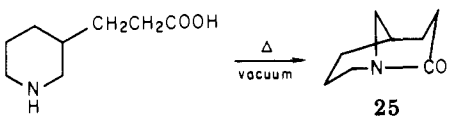


23 24

3.3.1 System. Hall, Shaw, and Deutschmann[32] synthesized 1-azabicyclo[3.3.1]nonan-2-one (**25**) in 7% yield by dehydrating amino acid **17** by heating from 180 to 285°C under high vacuum.



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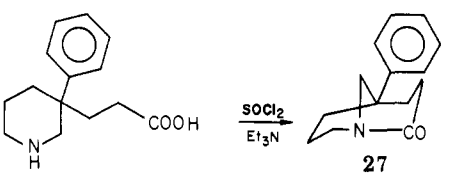
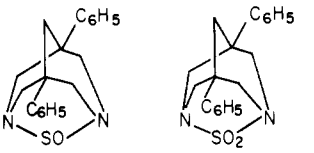
Most recently, Buchanan synthesized 5-phenyl-1-azabicyclo[3.3.1]nonan-2-one (**27**) in 10% yield.[33]



26 27

B. Ureas

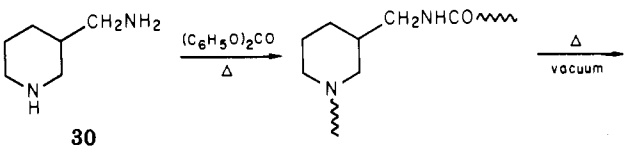
Simple N-bridgehead ureas were not found in earlier literature. The problem of synthesizing such ureas is not trivial, as shown by the work of Misito and Chiavarelli.[34] Although they readily obtained compounds **28** and **29** from the parent diamine, these investigators



28 29

showed that the corresponding urea was not formed under similar conditions.

The parent N-bridgehead urea **32** of the bicyclo-[3.3.1]nonane group was synthesized by Hall, Ekechukwu, Deutschmann, and Rose.[35] Diamine **30** reacted with diphenyl carbonate with heating to give linear polyurea **31**. Depolymerization by heating under vacuum gave **32**.



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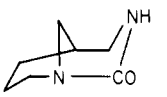

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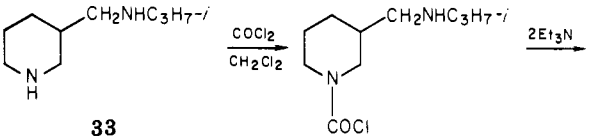
The 3-isopropyl analogue **35** was synthesized in 50% yield by the reaction of diamine **33** with phosgene in dichloromethane at 0 °C, followed by the addition of 2 equiv of triethylamine.[36] In ether the product was



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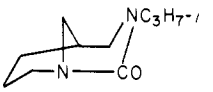
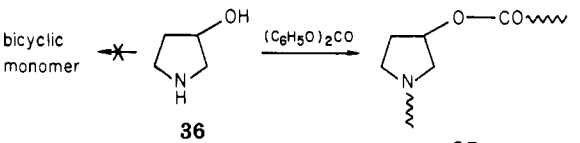


35

largely **34**, which could be converted to **35** by silver carbonate in refluxing acetonitrile.

C. Urethanes

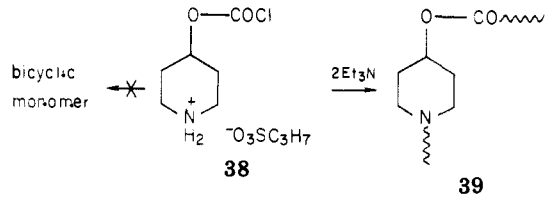
Heating 3-hydroxypyrrolidine (**36**) with diphenyl carbonate gave only linear polyurethane and no N-bridgehead bicyclic urethane.[25] Similarly, Schaefgen,



36 37

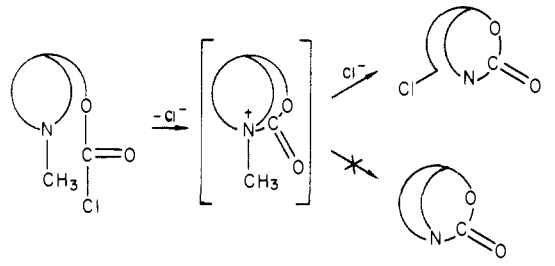
Koontz, and Tietz[37] obtained only linear polyurethane **39** and no bicyclic monomer from the chloroformate of 4-hydroxypiperidine (**38**). The diphenyl carbonate method also did not give bicyclic product.[24]

Fielden, Welstead, and Lunsford[38] and Li and Biel[39] showed that chloroformates derived from cyclic *N*-

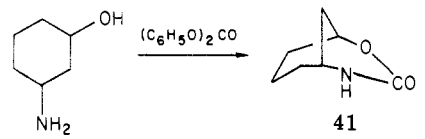


38 39

methylamino alcohols by reaction with phosgene, isomerized to chloroalkyl monocyclic urethanes by way of the quaternary ions of nitrogen-bridgehead bicyclic urethanes:



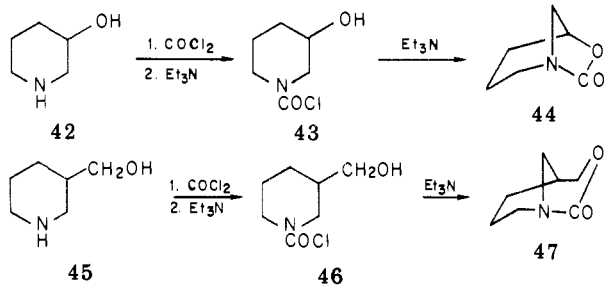
In no case did chloride ion dealkylate the ammonium salt with formation of the alkyl chloride and the N-bridgehead bicyclic urethane. That the anti-Bredt feature is responsible for these results is attested by the ready formation of a bicyclic urethane **41** without a nitrogen bridgehead.[24]



40 41

The first successful synthesis of N-bridgehead bicyclic urethanes proceeded from the corresponding cyclic secondary amino alcohols.[40]

The secondary amino alcohols **42** and **45** reacted with phosgene in dichloromethane at −30 °C in the presence of 1 equiv of triethylamine to give the hydroxy-carbamoyl chlorides **43** and **46**, owing to the much greater nucleophilicity of the amino group than the alcohol group. To bring about cyclization, the hydroxy carbamoyl chlorides were treated with 1 equiv of triethylamine in inert solvents.

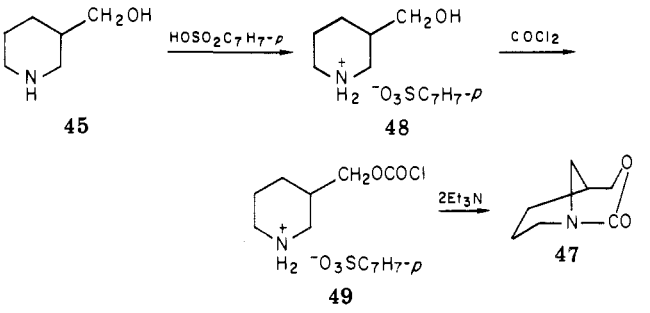


42 43 44

45 46 47

The [3.3.1] derivative **47** was obtained in 28% yield under mild conditions. More vigorous conditions were required to form the [3.2.1] urethane **44**, but then a 61% yield was achieved.

Alternatively, the nucleophilic nitrogen in **45** was protected by protonation. The amino alcohol was converted to the crystalline hydrotosylate. Phosgenation of the salt was carried out by using 1.0–1.5 equiv of phosgene in dichloromethane or chloroform at 0 °C. Treatment of the chloroformate salt **49** in dichloromethane with 2 equiv of triethylamine to liberate the amino chloroformate gave **47** in 75% yield.

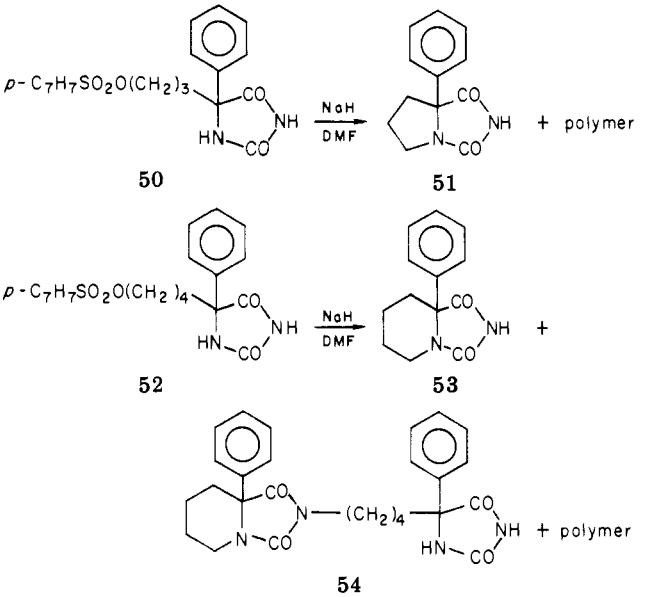


45 48 49 47

D. N-Bridgehead Hydantoins and Barbituric Acids

In an interesting series of papers Smissman and his colleagues have reported on N-bridgehead hydantoins and 2,4-oxazolidinediones, with the aim of synthesizing novel medicinal chemicals such as stereoselective anticonvulsant agents and antileptic drugs.

Smissman, Chien, and Robinson[41] found that, although hydantoins usually alkylate on the imide NH (N_3), compound **50** and **52** internally mostly alkylate the amide NH (N_1) to give isolated bond-bridged bicyclics **51** and **53**, the latter in very low yield (2.5%).



50 51

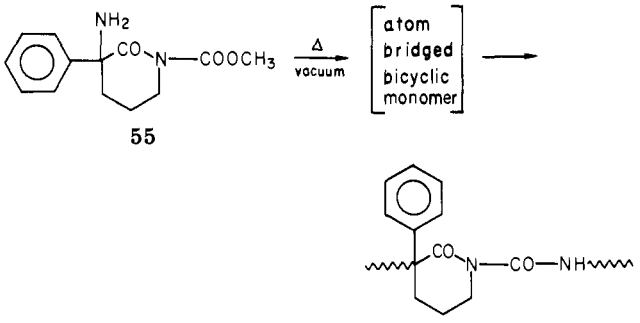
52 53

54

The authors ascribe the polymer formation, for which no experimental data were provided, to intermolecular polycondensation and isolated the dimer **54** in the second reaction. However, the atom-bridged bicyclics may also have formed by alkylation at N_3 and subsequently polymerized under the reaction conditions, inasmuch as NaH–DMF was used, and the hydantoins are themselves *N*-acyl cocatalysts for anionic polymerization.[18]

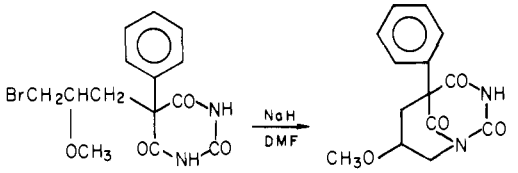
Using intramolecular acylation rather than alkylation as the final ring-forming step, Brouillette, Smissman, and Grunewald[42] tried to cyclize **55** but only obtained polymer. The authors propose a polymer with a hydantoin moiety. According to the reviewers, ring-opening polymerization of a labile bicyclic hydantoin would yield polymer **56**.

Smissman, Robinson, Carr, and Matuszak[43] turned to the synthesis of bridged barbituric acids and accom-



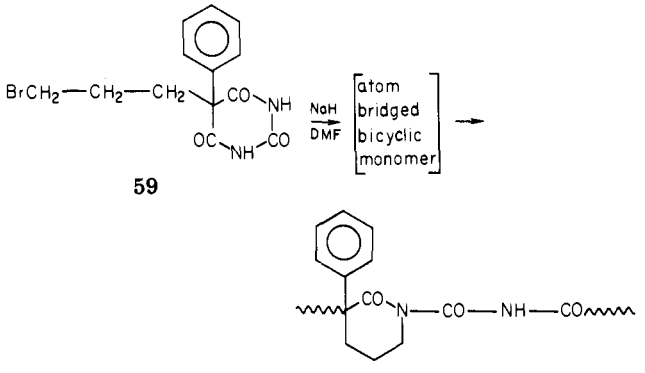
55 56

plished the following internal alkylation:



57 58

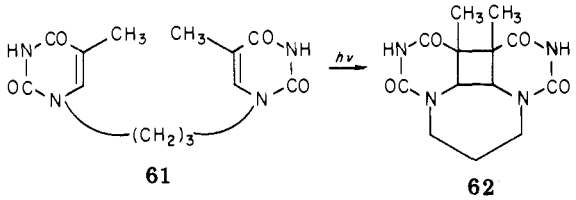
It seems that a methoxy group is necessary. When Smissman, Robinson, and Matuszak[44] tried to cyclize compound **59** lacking an OCH_3 group via NaH–DMF, only polymer was obtained. The authors attributed



59 60

this to intermolecular alkylation. However, the reviewers again think that anionic ring-opening polymerization of the desired atom-bridged bicyclic barbituric acid may have taken place under these conditions.

A photochemical high-energy route to novel multicyclic thymine derivatives was taken by Leonard and Golankiewicz[45], who photolyzed 1,1′-trimethylenebis-[thymine] **61** to the dimer **62**:

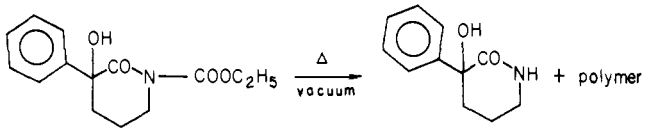


61 62

This reaction has been systematically studied and extended by Golankiewicz and his colleagues (see ref 46 for a review and also later articles in this series). However, it is unlikely that these multicyclic caged structures will undergo ring-opening polymerization.

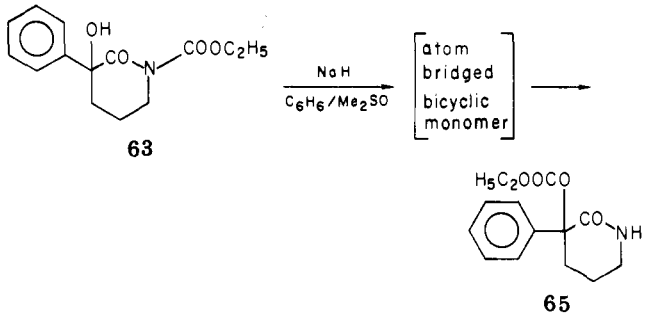
E. N-Bridgehead 2,4-Oxazolidinediones

Brouillette, Smissman, and Grunewald[42] did not succeed in carrying out the internal acylative ring closure of **63** to form an N-bridgehead 2,4-oxazolidinedione. Decarboethoxylation to **64** occurred along with polymer formation. Perhaps condensation polymeri-



63 64

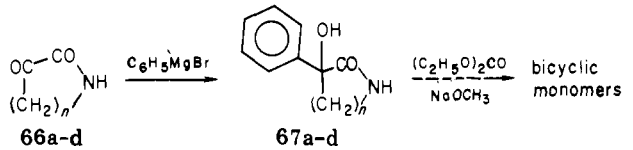
zation occurred under these conditions or again ring-opening polymerization of the desired bicyclic compound. The latter theory is partially supported by the mechanism proposed by the authors for an attempted base-catalyzed ring closure of **63**. Intramolecular eth-



63 65

oxycarbonyl migration occurs and the atom-bridged bicyclic 2,4-oxazolidinedione is proposed as an intermediate.

Brouillette[47] recently reported a further study of the synthesis of N-bridgehead 2,4-oxazolidinediones



66a-d, n = 1-4 67a-d, n = 1-4

IV. Physical Properties and Conformations of Bridgehead N—C=O Compounds

A. Infrared Spectra

The infrared absorption frequency of the carbonyl group for the various anti-Bredt-N-bridgehead compounds affords a preliminary indication of the extent to which the N—C=O resonance is inhibited.

Lactams. The carbonyl absorption frequency of 1-azabicyclo[3.3.1]nonan-2-one (**25**) lies at 1680 cm^{-1},[32] and the one for the corresponding 5-phenyl lactam **27** lies at 1695 cm^{-1}.[33] These are normal for tertiary amides. These amides adjust to the strain by transforming themselves into the chair–boat form. The absorption frequency of 1-azabicyclo[2.2.2]octan-2-one (**20**) at 1733 cm^{-1} is shifted about 40 cm^{-1} to higher wave length;[31] this amide group is significantly altered by Bredt's rule. The ability of bicyclo[3.3.1]non-1-ene (**1**) to exist as a stable molecule while bicyclo[2.2.2]oct-1-ene (**5**) has only been detected as a transient intermediate, is in keeping with these results.

Ureas. 1,3-Diazabicyclo[3.3.1]nonan-2-one (**32**) and its *N*-isopropyl derivative **35** absorbed infrared radiation at 1660 cm^{-1} and 1650 cm^{-1}, respectively. By comparison with the values of 1695 cm^{-1} for hexahydropyrimidinone and 1678 cm^{-1} for the isomeric 2,4-diazabicyclo[3.3.1]nonan-3-one, these are normal

values for cyclic six-membered ureas.

Urethanes. The anti-Bredt urethane, 1-aza-3-oxabicyclo[3.2.1]octan-2-one (**43**), absorbed at 1770 cm^{-1}. In comparison with 1-aza-3-oxa-bicyclo[4.3.0]nonan-2-one, another five-membered urethane (1750 cm^{-1}) this is normal.

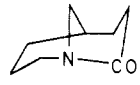
The six-membered urethane 1-aza-3-oxabicyclo-[3.3.1]nonan-2-one (**47**) absorbed 1710 cm^{-1}, close to the value of 1686 cm^{-1} reported for the isomeric 2-aza-4-bicyclo[3.3.1]nonan-3-one.

To summarize, the carbonyl absorptions are normal for every anti-Bredt molecule except the Pracejus [2.2.2] lactam. No correlation with polymerization tendency is found.

B. NMR Spectra

The conformation of two bicyclic lactams have been deduced from their NMR spectra.

The NMR spectrum of the [3.3.1] lactam **25** was consistent with the structural assignment.[32] The most



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significant feature was a doublet for one hydrogen at δ 4.10. This downfield absorption was explained by its assignment to the equatorial hydrogen at C(8). In the chair–boat conformation this hydrogen is in the anisotropic cone of the carbonyl group.

In an alternative NMR approach, the ^1H NMR spectrum of 5-phenyl-1-aza-bicyclo[3.3.1]nonan-2-one (**27**) reveals W coupling between one of the C(9) protons and the equatorial protons on C(6) and C(8). The absence of W coupling involving the H at position 4 again indicated a boat–chair conformation for this bicyclic lactam **33**.

Thus, these molecules adopt chair–boat structures, as expected from the comments of Chong and Wiseman. This conformation is energetically reasonable: the amide resonance stabilization energy, about 20 kcal mol^{-1}, is greater than the energy required to force a cyclohexane ring into the boat form, about 12 kcal mol^{-1}.[30]

Little work on the anti-Bredt ureas and urethanes has been presented as yet.

V. Chemical Reactivities and Strains of Bridgehead N—C=O Compounds

A. Ring-Opening Polymerization

Lactams. The bicyclo[2.2.2] lactam **20** partially polymerized during sublimation at 40–65 °C.[29-31] The bicyclo[3.3.1] lactam **25** possesses a six-membered ring in the boat conformation, and it polymerized when heated to 100 °C with phosphoric acid.[32]

Ureas. The parent [3.3.1] urea **32** thermally polymerized readily at **125** °C or with phosphoric acid at 98 °C.[35] The N-substituted [3.3.1] urea **35** showed no signs of polymerization after heating for extended periods with various initiators.[36] This is similar to the inhibiting effect of substituents described for ring-opening polymerization of monocyclic compounds.

Urethanes. The [3.2.1] derivative **43** readily polymerized in high yields when heated at 112–131 °C with various initiators, including dibutyltin oxide, potassium *tert*-butoxide, *p*-toluenesulfonic acid, and phenylphosphonic acid.[49] The [3.3.1] urethane **46** underwent polymerization by heating at 150 °C with dibutyltin oxide or *p*-toluenesulfonic acid.[50]

Hydantoins, Barbituric Acids, and Oxazolidinediones. Polymerizations of the synthesized compounds have not been reported as this work has been done by chemists interested in medicinal application. The polymers observed in the attempted syntheses nevertheless indicate the possibilities.

To summarize, ring-opening polymerization is a very sensitive technique to detect ring strain in monocyclic and bicyclic molecules. All anti-Bredt compounds (except the *N*-isopropyl derivative) polymerized. In this they differed from their homomorphic isomers lacking the anti-Bredt feature.

B. Hydrolysis

Lactams. The bicyclic[2.2.2] lactam **20** hydrolyzed in water at 20 °C with a half-life of 16 min and ethanolyzed with a half-life of 12 h.[29-31] The bicyclic-[3.3.1]lactam **25** is stable in boiling water, but hydrolyzed rapidly when treated with dilute hydrochloric acid at room temperature.[32]

Ureas. The parent bicyclic[3.3.1] urea **32** did not react significantly with water at 70 °C or with dilute potassium hydroxide at 70 °C in two h. However, introduction of hydrogen chloride in an aqueous solution gave immediate hydrolysis.[35]

The N-substituted [3.3.1] urea **35** is stable to boiling water for 20 h, but hydrolyzed slowly in hot sodium hydroxide solution.[36]

Urethanes. The [3.3.1] derivative **47** is soluble and stable in water, but the [3.2.1] derivative **44** is not. These two bicyclic urethanes are completely stable to potassium *tert*-butoxide and to *p*-toluenesulfonic acid monohydrate.[40]

To summarize, quantitative studies will be needed before conclusions can be drawn.

C. Basicity

Pracejus found the pK_a of quinuclidone-2 **20** to be 5.33, actually slightly more basic than aniline or pyridine. In contrast, normal amides show pK_a values between +0.84 and −0.63. This was taken as powerful evidence for localization of the electron pair on nitrogen.[29-31]

VI. Conclusions

Bredt's Rule definitely influences the synthesis and stability of the N-bridgehead bicyclic compounds, because the resonance stabilization of the amide function is prohibited. This is most apparent in the lactam series in which the anti-Bredt feature definitely destabilizes the [2.2.2] compounds. The anti-Bredt feature destabilized the [3.3.1] compounds too, not in the expected way, but by forcing it into a chair–boat conformations in agreement with Wiseman's Rule. An adjacent nitrogen or oxygen made the synthesis of the bicyclic N-bridgehead ureas and urethanes, respectively, easier. Partial resonance stabilization is provided by the added hetero atom, and these compounds are more stable than the lactams.

Nevertheless, the successful synthesis methods have started from high energy intermediates such as carbamoyl chlorides or by thermolytic depolymerization, indicating high energy levels of these bicyclic compounds.

VII. Outlook

The future appears bright for the synthesis and systematic study of new N-bridgehead anti-Bredt molecules. It is apparent that many more of these interesting compounds can be synthesized by using established techniques.

A more systematic study of polymerizations is also very attractive, inasmuch as these compounds result in novel polymers with possibly unique properties.

Smissman and his colleagues have attempted syntheses for N-bridgehead bicyclic hydantoins, barbituric acids, 2,4-oxazolidinediones, etc., with the purpose of obtaining novel drugs. This area is also open for more investigation.

Finally, the stereoelectronic aspects of hydrolysis at C=O carbon[51] may be illuminated by systematic study of these molecules.

VIII. References

( ) Bredt, J. *Liebigs Annl. Chem.* **1924**, *437*, 1.
(2) Marshall, J. A.; Faubl, H. *J. Am. Chem. Soc.* **1970**, *92*, 948.
(3) Wiseman, J. R.; Pletcher, W. A. *J. Am. Chem. Soc.* **1970**, *92*, 956.
(4) Becker, K. B. *Helv. Chim. Acta* **1977**, *60*, 81.
(5) Wiseman, J. R.; Chan, H. F.; Ahola, C. J. *J. Am. Chem. Soc.* **1969**, *91*, 2812.
(6) Keese, R.; and Krebs, E. P. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 262; **1972**, *11*, 518.
(7) Grootveld, H.; Blomberg, C.; Bickelhaupt, F. *J. Chem. Soc., Chem. Commun.* **1973**, 542.
(8) Wolf, A. D.; Jones, M. *J. Am. Chem. Soc.* **1973**, *95*, 8209.
(9) Chong, J. A.; Wiseman, J. R. *J. Am. Chem. Soc.* **1972**, *94*, 8627.
(10) Reed, J. O.; Cwowski, W. *J. Org. Chem.* **1971**, *36*, 2864.
(11) Koebrich, G. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 464.
(12) Toda, M.; Hirata, Y.; Yamamura, S. *Chem. Commun.* **1970**, 1597.
(13) Grob, C. A.; Sieber, A. *Helv. Chim. Acta* **1967**, *50*, 2531.
(14) Buchanan, G. L. *Chem. Soc. Rev.* **1974**, *3*, 41.
(15) Liebman, J. F.; Greenberg, A. "Strained Organic Molecules"; Academic Press: New York, 1978.
(16) Szeimies, G. *React. Intermed. (Plenum)* **1983**, *3*, 299.
(17) Lukes, R. *Collect. Czech. Chem. Commun.* **1939**, *10*, 148.
(18) Hall, H. K., Jr. *J. Am. Chem. Soc.* **1958**, *80*, 6404.
(19) Carothers, W. H. *Chem. Rev.* **1930**, *8*, 353.
(20) Dainton, F. S.; Ivin, K. J. *Q. Rev., Chem. Soc.* **1958**, *12*, 61.
(21) Small, P. A. *Trans. Faraday Soc.* **1953**, *49*, 441.
(22) Frisch, K. C.; Reegan, S. L., Eds. "Ring-Opening Polymerization"; Marcel Dekker: New York, 1969.
(23) Goethals, E. J.; Saegusa, T. *ACS Symp. Ser.* **1977**, *No. 59*.
(24) Ivin, K. J.; Saegusa, T. "Ring-Opening Polymerization"; Applied Science Publishers: Barking, U.K., in press.
(25) Hall, H. K., Jr. *J. Am. Chem. Soc.* **1958**, *80*, 6412.
(26) Hall, H. K., Jr., *J. Am. Chem. Soc.* **1960**, *82*, 1209.
(27) Yakhontov, L. N.; Rubsitov, M. V. *J. Gen. Chem. USSR (Engl. Transl.)* **1957**, *27*, 83.
(28) Yakhontov, L. N. *Russ. Chem. Rev. (Engl. Transl.)* **1969**, *38*, 470.
(29) Pracejus, H. *Chem. Ber.* **1959**, *92*, 988.
(30) Pracejus, H. *Chem. Ber.* **1965**, *98*, 2897.
(31) Pracejus, H.; Kehlen, M.; Kehlen, H.; Matschiner, H. *Tetrahedron*, **1965**, *21*, 2257.
(32) Hall, H. K., Jr.; Shaw, R. R.; Deutschmann, A., Jr. *J. Org. Chem.* **1980**, *45*, 3722.
(33) Buchanan, G. L. *J. Chem. Soc., Chem. Commun.* **1981**, 814.
(34) Misito, D.; Chiavarelli, S. *Gazz. Chim. Ital.* **1966**, *96*, 1696; *Chem. Abstr.* **1966**, *66*, 85777.
(35) Hall, H. K., Jr.; Ekechuchwu, O. E.; Deutschmann, A., Jr.; Rose, C. *Polym. Bull.* **1980**, *3*, 375.
(36) Hall, H. K., Jr.; Johnson, R. C. *J. Org. Chem.* **1972**, *37*, 697.
(37) Shaefgen, J. R.; Koontz, F. H.; Tietz, R. F. *J. Polym. Sci.* **1959**, *40*, 377.
(38) Fielden, M. L.; Welstead, W. J.; Lunsford, C. *Abstr. Pap.—Am. Chem. Soc.* **1966**, *152nd*, 15.
(39) Li, J. P.; Biel, J. H. *J. Org. Chem.* **1970**, *35*, 4100.
(40) Hall, H. K., Jr.; El-Shekeil, A. *J. Org. Chem.* **1980**, *45*, 5325.
(41) Smissman, E. E.; Chien, P. L.; Robinson, R. A. *J. Org. Chem.* **1970**, *35*, 3818.
(42) Brouillette, W. J.; Smissman, E. E.; Grunewald, G. L. *J. Org. Chem.* **1979**, *44*, 839.
(43) Smissman, E. E.; Robinson, R. A.; Carr, J. B.; Matuszak, A. J. B. *J. Org. Chem.* **1970**, *35*, 3821.
(44) Smissman, E. E.; Robinson, R. A.; Matuszak, A. J. B. *J. Org. Chem.* **1970**, *35*, 3823.
(45) Leonard, N. J.; Golankiewicz, K.; McCredie, R. S.; Johnson, S. M.; Paul, I. C. *J. Am. Chem. Soc.* **1969**, *91*, 5855.
(46) Golankiewicz, K. *Heterocycles* **1977**, *7*, 429.
(47) Brouillette, W. J. *Abstr. Pap.—Am. Chem. Soc.* **1982**, *184th*, ORGN 215.
(48) Hall, H. K., Jr.; Zbinden, R. *J. Am. Chem. Soc.* **1958**, *80*, 6428.
(49) Hall, H. K., Jr.; El-Shekeil, A. *Polym. Bull.* **1980**, *2*, 829.
(50) Hall, H. K., Jr.; El-Shekeil, A. *Polym. Bull.* **1981**, *3*, 233.
(51) Deslongchamps, P. *Heterocycles* **1977**, *7*, 1271.