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.), $n^{25}D$ 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°, $n^{25}D$ 1.4316. Redistillation gave a distillate (b.p. 100–104° (20 mm.), $n^{25}D$ 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 $C_4H_8ON_2$: 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 $C_6H_{10}O_3$: 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 $C_5H_{12}O_3$: C, 58.3; H, 8.4. Found: C, 58.3, 58.6; H, 8.8, 8.8.

N-Acetylethyleneurea 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.

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

(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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[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.

RECEIVED JUNE 30, 1958

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 I[3] and 2-azabicyclo-[3:2:2]nonan-3-one II[4] when heated with water

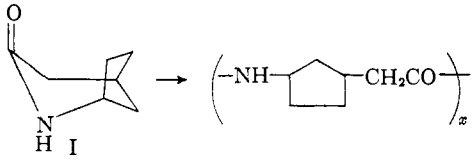
(1) H. K. Hall, Jr., THIS JOURNAL, **80**, 6404 (1958).

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

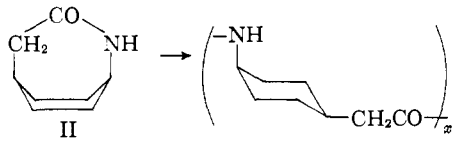
(3) Swiss Patent 270,546 (1951), to Inventa A. G. Lucerne; *cf.* A. J. Hall, *Fibers*, **18**, 402 (1957).

(4) Swiss Patents 276,924 (1951); 280,367 (1952).

were converted to polyamides

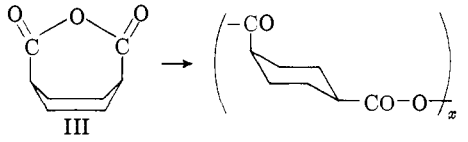


I



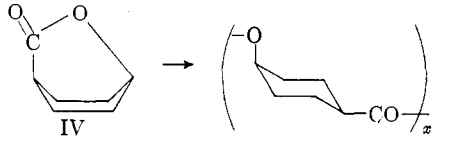
II

Similarly, *cis*-1,4-cyclohexanedicarboxylic anhydride, 3-oxabicyclo[3:2:2]nonane-2,4-dione (III), was polymerized by[5,6] traces of water



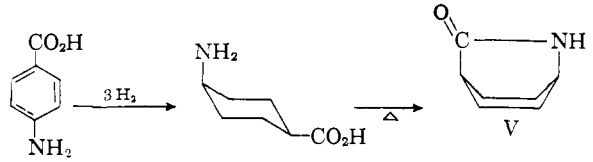
III

Lastly, the lactone of *cis*-4-hydroxycyclohexanecarboxylic acid, 2-oxabicyclo[2:2:2]octan-3-one (IV), can be polymerized by heating with phosphoric acid[6,7]

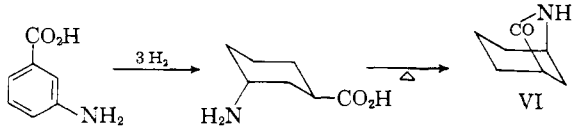


IV

Preparation of Monomers—Lactams.—The lactams 2-azabicyclo[2:2:2]octan-3-one (V) and 6-azabicyclo[3:2:1]octan-7-one (VI) were readily prepared by literature methods[8-11]

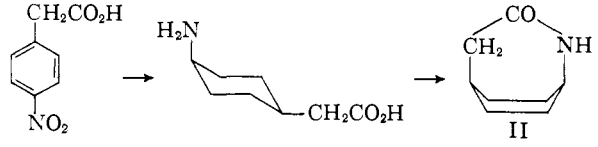


V



VI

Hydrogenation of *p*-nitrophenylacetic acid over ruthenium proceeded smoothly to yield 4-aminocyclohexylacetic acid



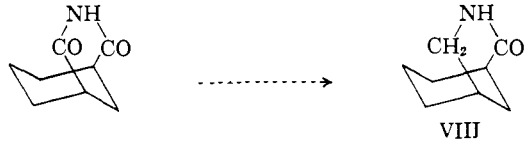
II

When heated at 250° at 15 mm. it polymerized and no lactam was detected. When heated at 150 mm. with a flame, however, all of the material distilled. Redistillation gave two fractions, from the higher-boiling of which a small amount of the crystalline lactam 2-azabicyclo[3:2:2]nonan-3-one (II) could be isolated. Therefore this preparation is much inferior to that involving rearrangement of bicyclooctanone oxime.[4] It is noteworthy that the corresponding isomer forms very readily when the 1,3-aminoacid or aminoester is heated.[12,13]

Tetrahydrophthalimide was hydrogenolyzed over Raney nickel in cyclohexane at 210°.[14,15] The product was a mixture of the lactam and unreacted imide, which was eliminated by crystallization and by selective hydrolysis with alkali. The pure lactam 2-azabicyclo[4:3:0]nonan-1-one (VII) was crystallized from the unreacted remainder.

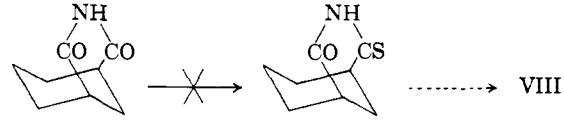
VII

Attempts to hydrogenolyze cyclohexane-1,3-dicarboximide (see below) to 2-azabicyclo[3:3:1]-nonan-3-one (VIII) led largely to unreacted starting material. The lactam was not isolated. However, the selective purification by alkali was not tried.



VIII

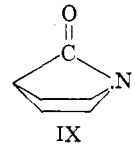
Reduction of the imide with a limited amount of lithium aluminum hydride failed to give VIII. Attempted selective conversion to the monothioimide



with a view to subsequent desulfuration, gave unreacted imide as the only isolable substance.

Future attempts to reduce these and other imides might better be attempted by electrolytic reduction, which has been used in the past in this connection.[16]

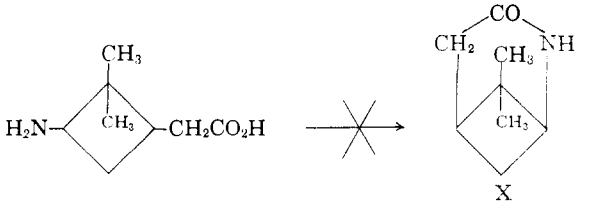
Heating piperidine-4-carboxylic acid with a free flame resulted only in sublimation of the amino-acid. No lactamization to 1-azabicyclo[2:2:1]-heptan-7-one (IX) or polymerization was noted.[17]



IX

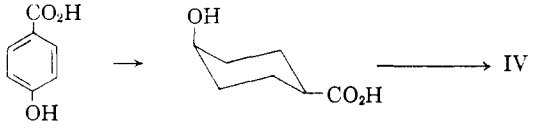
No 2-aza-6,6-dimethylbicyclo[3:1:1]heptan-3-one was obtained from 2,2-dimethyl-3-aminocyclobutaneacetic acid on similar treatment

(5) R. Malachowski and J. Jankiewicsowna, *Ber.*, **67**, 1783 (1934).
(6) Dr. A. K. Schneider, these laboratories, unpublished work.
(7) H. Batzer and G. Fritz, *Makromol. Chem.*, **14**, 213 (1954).
(8) F. R. Hewgill and P. R. Jefferies, *J. Chem. Soc.*, 2767 (1955).
(9) J. Houben and A. Pfau, *Ber.*, **49**, 2297 (1916).
(10) G. Wendt, *ibid.*, **75**, 425 (1942).
(11) E. Ferber and H. Brueckner, *ibid.*, **76**, 1019 (1943).
(12) M. W. Cronyn, *J. Org. Chem.*, **14**, 1013 (1949).
(13) D. Ginsburg, *ibid.*, **15**, 1003 (1950).
(14) B. Wojcik and H. Adkins, THIS JOURNAL, **56**, 2419 (1934).
(15) J. Paden and H. Adkins, *ibid.*, **58**, 2487 (1936).
(16) S. Swann in "Catalytic, Photochemical, and Electrolytic Reactions," A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1956, p. 505.
(17) Dr. J. R. Schaefgen, unpublished work, these laboratories.

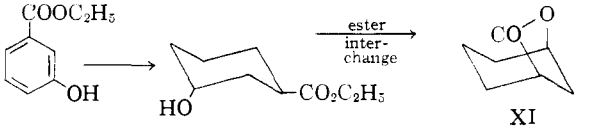


X

Lactones.—2-Oxabicyclo[2:2:2]octan-3-one (IV) was prepared readily by hydrogenation of *p*-hydroxybenzoic acid, followed by dehydration, as described in the literature[18-20]

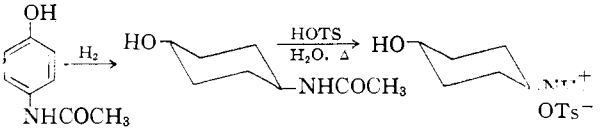


An attempt to prepare 6-oxabicyclo[3:2:1]octan-7-one (XI) gave a product which was very difficult to purify. An alternate route was found *via* ester interchange.[6]

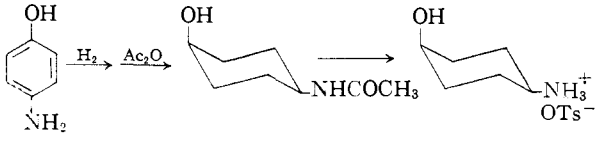


XI

Urethans.—The stereochemically homogeneous aminoalcohols were required. Previous investigators[21,22] have described the hydrogenation of *p*-acetylaminophenol and the separation of the product into *cis* and *trans* isomers by fractional crystallization. We found that the higher-melting *trans* isomer was easily accessible by this means, but that the *cis* isomer could be isolated only with difficulty. The latter was obtained satisfactorily by hydrogenating *p*-aminophenol, acetylating, and crystallizing. *cis*-1,3-Acetylaminocyclohexanol was obtained from hydrogenation of the corresponding phenol.[23]

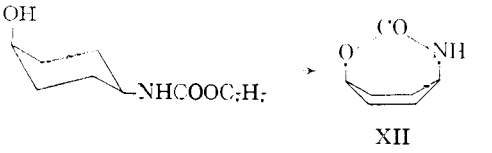


(1,3-isomer obtained similarly)



Hydrolysis of the acetyl groups from the pure isomers was accomplished by toluenesulfonic acid in water giving pure crystalline hydrotosylates of the aminocyclohexanols.

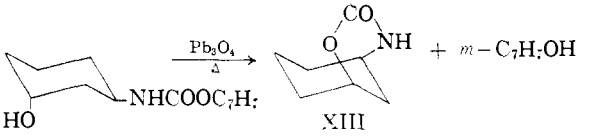
Treatment of *cis*-4-aminocyclohexanol hydrotosylate with *m*-cresyloxycarbonyl chloride gave the *m*-cresyloxycarbonyl derivative, which when heated with litharge gave the bicyclic urethan 2-oxa-4-azabicyclo[3:2:2]nonan-3-one (XII) in low yield



XII

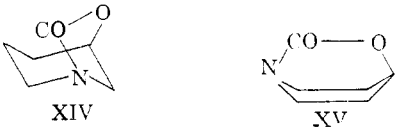
An attempt to cyclize the N-benzyloxycarbonyl derivative of *cis*-4-aminocyclohexanol with phosgene[24] failed.

The bicyclic urethan 2-oxa-4-azabicyclo[3:3:1]-nonan-3-one (XIII)[23] from *cis*-3-aminocyclohexanol is easily prepared in quantity similarly.



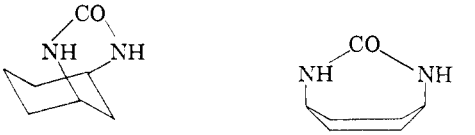
XIII

The urethans 1-aza-6-oxabicyclo[3:2:1]octan-7-one (XIV) and 1-aza-3-oxabicyclo[2:2:2]octan-2-one (XV) could not be obtained by this method, starting from 3- and 4-hydroxypiperidine.



XIV XV

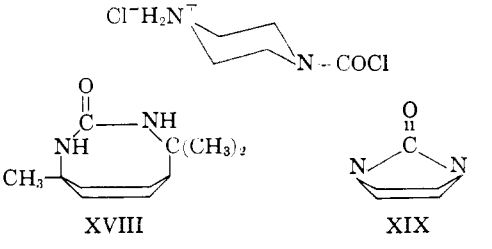
Ureas.—1,3-Diaminocyclohexane, on treatment with diethyl carbonate, followed by sublimation, gave 2,4-diazabicyclo[3:3:1]nonan-3-one[25] (XVI).



XVI XVII

The 1,4-diaminocyclohexane, on similar treatment, failed to give 2,4-diazabicyclo[3:2:2]nonan-3-one (XVII).

The reaction of 1,8-diamino-*p*-menthane with diphenyl carbonate gave polymer directly, and no bicyclic urea XVIII was obtained. The reaction of piperazine with excess phosgene[26] gave only the salt of the monocarbamyl chloride and polyurea.



XVIII XIX

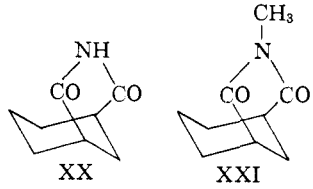
Imides.—The imide of *cis*-cyclohexane-1,3-dicarboxylic acid, 3-azabicyclo[3:3:1]nonane-2,4-dione (XX), readily was prepared by distilling a mixture of the acid with ammonium hydroxide.[27] The N-methylimide XXI was prepared analogously.

(18) M. Kilpatrick and J. G. Morse, THIS JOURNAL, **75**, 1847 (1953).
(19) H. L. Goering and C. Serres, Jr., *ibid.*, **74**, 5908 (1952).
(20) D. S. Noyce and H. Weingarten, *ibid.*, **79**, 3101 (1957).
(21) British Patent 454,042 (1936)
(22) E. Ferber and H. Brueckner, *Ber.*, **72**, 995 (1939).
(23) R. R. Burford, F. R. Hewgill and P. R. Jefferies, *J. Chem. Soc.*, 2937 (1957).
(24) D. Ben-Ishai, THIS JOURNAL, **78**, 4962 (1956).
(25) F. R. Hewgill and P. R. Jefferies, *J. Chem. Soc.*, 805 (1956).
(26) Dr. A. H. Frazer, unpublished work, these laboratories.
(27) G. Komppa, *Ber.*, **65**, 792 (1932).

TABLE I

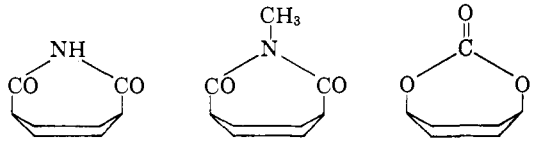
POLYMERIZATIONS OF BICYCLIC MONOMERS

Monomer	Wt., g.	Catalyst	Additive	Time	Temp., °C.	Polymer wt., g.	Polymer m.p., °C.	Polymer inherent viscosity
V	2.36	H_2O, 0.04 g.	.....	16 hr.	200	0	...	.....
	4.0	NaH, 0.15 g.	N-Acetylcaprolactam, 0.11 g.	1.5 hr.	260	0.84	>400	0.38 (sulfuric)
VI	4.0	H_2O, 0.04 g.	.....	16 hr.	200	0	...	.....
	40.0	NaH, 0.25 g.	.....	10 min.	210	30	>400	.41 (sulfuric)
IV	4.0	Na dispersion, 1 drop	.....	20 hr.	150	0.60	195	.40 (cresol)
XI	4.0	Na dispersion, 1 drop, or 0.05 g. Pb_3O_4	.....	92 hr.	150	3.60	75	.04 (acetone)
XII	4.0	Pb_3O_4, 0.05 g.	.....	1 hr.	150	3.60	170	.06 (acetone)



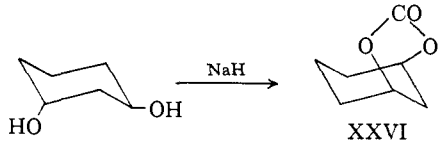
XX XXI

Attempts to prepare the corresponding imides of cyclohexane-1,4-dicarboxylic acid XXII and XXIII met with no success.



XXII XXIII XXVII

Carbonates.—The cyclic carbonate of cyclohexane-1,3-diol, 2,4-dioxabicyclo[3:3:1]nonan-3-one XXVI was prepared by the reaction of the diol with diethyl carbonate, catalyzed by sodium hydride



XXVI

Cyclohexane-1,4-diol gave a low yield of bicyclic carbonate, 2,4-dioxabicyclo[3:2:2]nonan-3-one (XXVII), contaminated with unreacted diol.

Anhydrides.—*cis*-Cyclohexane-1,3-dicarboxylic anhydride, 3-oxabicyclo[3:3:1]nonane-2,4-dione (XXVIII), was obtained readily by the method of Perkin.[28,29]

Polymerizations were carried out using catalysts previously found appropriate for the various types of rings.[1,2] Details are given below and the results in Table I.

Correlation of Bridged Ring Structure with Polymerizability.—The results are summarized in Table II. As before, it is assumed that the catalysts employed were sufficiently powerful to establish equilibrium between monomer and polymer.

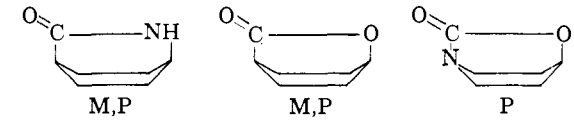
In the bicyclic series, different types of monomer belonging to a given ring system show common behavior. A straightforward interpretation of their behavior in conformational terms can be made although the reasons for the contrast between the mono- and bicyclic monomers is unknown.

(28) W. H. Perkin, Jr., *J. Chem. Soc.*, **59**, 812, 816 (1891).
(29) W. Goodwin and W. H. Perkin, Jr., *ibid.*, **87**, 849 (1905).

TABLE II

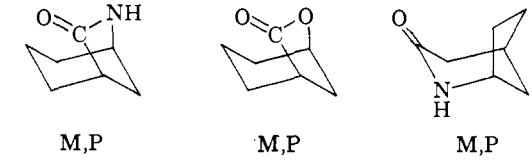
POLYMERIZABILITY OF BRIDGED BICYCLIC MONOMERS[a]

Bicyclic system 2:2:2



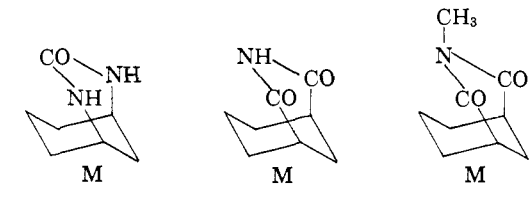
M,P M,P P

Bicyclic system 3:2:1



M,P M,P M,P

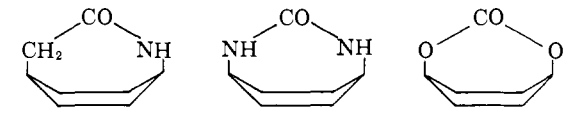
Bicyclic system 3:3:1



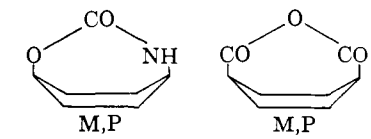
M M M

M M M

Bicyclic system 3:2:2



M,P P M,P

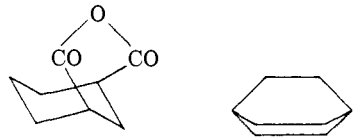


M,P M,P

[a] M and P denote that monomeric or polymeric forms, respectively, were obtained.

The bicyclo[2:2:2]octane system occurs in the two boat form which is slightly twisted[30] to relieve H–H interactions. Bicyclo[2:2:2]octene is strained

(30) R. B. Turner, W. R. Meador and R. E. Winkler, THIS JOURNAL, **79**, 4116 (1957).

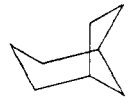


XXVIII

to the extent of 4 kcal.,[31] while bicyclo[2:2:2]octanone has been considered to be strainless.[32-34]

The polymerizations of lactam V and lactone IV show the presence of strain in the system, which is relieved on conversion to the polymeric chair form. The same effect continues in the bicyclo[3:2:2] system, where all of the monomers studied can be polymerized.

The bicyclo[3:2:1] system consists of a chair cyclohexane fused to a cyclopentane ring



The lactone XI polymerizes very sluggishly, and little strain is evident. The very ready polymerization of lactam VI is brought about by the requirement of coplanarity for nitrogen–carbonyl interaction. As in the unsubstituted 5-membered ring[1] this interaction can occur more effectively in the polymeric substance.

The bicyclo[3:3:1] system consists of two fused chairs, and no instability should exist. In agreement, none of the corresponding monomers could be polymerized. Therefore, the fact that the two chair forms are fused in the diaxial positions does not introduce appreciable strain. Other evidence supports this contention.[35-37]

2-Azabicyclo[3:3:1]nonan-3-one (XXIX)[38,39] was

XXX

not studied in this investigation. Both the conformation and reported ease of cyclization to form this lactam[1] lead us to predict that it will not polymerize.

Finally, Wittbecker[40] has shown that 7-oxabicycloheptane (XXX) undergoes ready polymerization. Together with the known strain in bicyclo[2:2:1] derivatives,[31] this indicates that other bicyclic monomers of this class will polymerize.

In an earlier article[1] rate of cyclization was considered to be the major factor governing polymerizability, while in the present article attention has been focused on strain in the monomer. The two viewpoints can be reconciled readily by the reasonable postulate that cyclization occurs most rapidly to form the least strained rings.

In Table III is given a very tentative summary of the various types of strain to be expected in various cyclic monomers. This may serve as a basis for future discussion. The statements are based on inspection of models, the polymerization results and statements in the cited literature.

TABLE III

TYPE OF STRAIN

Ring size	Angle	H–H or H-lone pair	Inhibition of N—C=O resonance in lactams, ureas
4	+	Small	+
5	0	+	+
6	0	− (lactam, urea, etc.) + (esters)	0
7	0	+	0
[2:2:1]heptane	+	+	+
[2:2:2]octane	0	+	*ca.* 0
[3:2:1]octane	0	0	+
[3:2:2]nonane	0	+	0
[3:3:1]nonane	0	0	0

Comparison of Catalysts.—The observation that water, even when promoted with other catalysts, fails to polymerize lactams V and VI, whereas sodium hydride polymerizes them readily is quite striking. For all other lactams which have been studied to date, these two catalysts have been equally effective. Even the bridged lactams I and II were polymerized by water.

The reason undoubtedly lies in the tightly caged structure which prevents rearward attack by the shell of water molecules on the carbonyl group.[41] The conformational formulas make it clear that V, and to some extent VI, is far more hindered in this respect than are I and II. As a corollary, in the alkali-catalyzed polymerization nucleophilic attack of the lactam anion must occur *via* a transition state of different configuration, one in which the anion approaches from the side or end of the molecule.

It must be pointed out that lactones IV and XI are both hydrolyzed by heating with water.[42] However, the mechanism of this reaction may be quite different from the lactam case.

Bridgehead Lactams and Urethans.[43-46]—Lukes[43] pointed out that lactams with nitrogen at the bridgehead will be difficult if not impossible to prepare. In such compounds the usual interaction $-\overset{\overset{O}{\|}}{C}-N< \leftrightarrow -\overset{\overset{O^-}{|}}{C}=\overset{+}{N}<$ cannot occur, since Bredt's rule would be violated. In fact no lactams of this type ever have been reported.

It occasioned no surprise, therefore, that we have been unable to prepare lactam IX, urea XIX, and

(31) P. von R. Schleyer, address at Delaware Valley Symposium, Philadelphia, Feb. 5, 1958; THIS JOURNAL, **80**, 1700 (1958).

(32) K. Alder and G. Stein, *Ber.*, **67**, 613 (1934).

(33) The data of Alder and Stein were compared with those of other bicyclic ketones listed by M. S. Kharasch, *J. Res. Natl. Bureau Stds.*, **2**, 387 (1929).

(34) However, W. R. Vaughan and A. C. Schoenthaler, THIS JOURNAL, **80**, 1956 (1958), have shown that dibenzo derivatives of bicyclo-[2:2:2] systems are prone to rearrange to bicyclo[3:2:1] compounds.

(35) H. Kwart and G. C. Gatos, THIS JOURNAL, **80**, 881 (1958).

(36) S. J. Angyal and D. J. McHugh, *J. Chem. Soc.*, 1473 (1957).

(37) A. Weissbach, *J. Org. Chem.*, **23**, 329 (1958).

(38) M. W. Cronyn, *ibid.*, **14**, 1013 (1949).

(39) D. Ginsburg, *ibid.*, **15**, 1003 (1950).

(40) E. L. Wittbecker, Abstracts of 129th A.C.S. Meeting, Dallas, Texas, April, 1956, p. 8R.

(41) D. H. G. Ballard and C. H. Bamford, *J. Chem. Soc.*, 355 (1958).

(42) R. R. Grewe, C. Heinke and C. Sommer, *Chem. Ber.*, **89**, 1978 (1956).

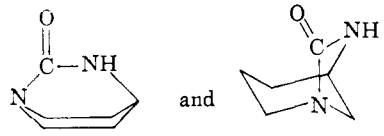
(43) R. Lukes, *Coll. Czech. Chem. Comm.*, **10**, 148 (1938).

(44) W. von E. Doering and J. D. Chanley, THIS JOURNAL, **68**, 586 (1946).

(45) F. S. Fawcett, *Chem. Revs.*, **47**, 258 (1950).

(46) Prof. C. A. Grob, private communication.

urethans XIV and XV. Failure of the latter indicates that oxygen cannot effectively donate electrons to the C=O group. This raises the interesting possibility that the bridgehead ureas



should prove capable of preparation.

Acknowledgments.—I am deeply indebted to Mr. H. E. Cupery and his associates for the many hydrogenations required in this work, to Mr. I. D. Plank and his associates for the microanalyses, to Mr. C. Mardecz and Mr. J. L. Sease for excellent technical assistance, and to Dr. P. W. Morgan for encouragement and inspiration.

Experimental

Lactams of 3- and 4-Aminocyclohexanecarboxylic Acids.—The 1,4-lactam and 1,3-lactam were prepared according to literature directions. The aminobenzoic acid was hydrogenated over ruthenium-on-charcoal in water solution. The solution was poured into acetone to precipitate the amino acid. It was filtered and distilled over a free flame. The lactams were crystallized from methyl isobutyl ketone–heptane. The 1,4-isomer melted at 195–196°, the 1,3-isomer at 195–197°.

Lactam of 4-Aminocyclohexylacetic Acid.—*p*-Nitrophenylacetic acid, 50 g., was hydrogenated in water solution over ruthenium dioxide. The catalyst was filtered, most of the water was evaporated under reduced pressure, and the product was precipitated with acetone. There was obtained 40.0 g. of white solid, m.p. *ca.* 290°, on a heated bar.[47]

Anal. Calcd. for $C_8H_{15}O_2N$: C, 61.1; H, 9.6. Found: C, 60.3; H, 9.5.

Heating this at 250° (15 mm.) for 1.5 hours gave no sublimate of lactam. More severe conditions were adopted. The aminoacid, 22.0 g., was heated with 1 drop of 85% phosphoric acid at 150 mm. with a pale blue flame. Water was evolved, leaving a viscous residue which distilled steadily to leave almost no residue. The distillate was dried azeotropically with benzene and was redistilled. This gave 2.50 g. of mobile liquid, b.p. 100–120° (15 mm.), and 3.40 g. of oily liquid, b.p. 160–180° (15 mm.). They were acidic and were neutralized with 1.0 *N* alkali, the former requiring 9 ml., the latter 2 ml. Extraction of the titration mixtures with ether, redistillation and infrared examination gave the following results. The lower-boiling fraction was a mixture of roughly equal amounts of an amide and a nitrile. The higher boiling material, 1.4 g., contained mostly lactam. It was crystallized from 1:1 hexane–ether to give 0.30 g. of white solid. Sublimation at 125° (0.25 mm.) gave 0.24 g. of white crystals, m.p. 124° on a heated bar.

Anal. Calcd. for $C_8H_{13}ON$: N, 10.1. Found: N, 10.0.

Hydrogenation of *p*-nitrophenylacetic acid over platinum in acetic acid gave a non-crystalline product which on distillation as above gave a complex mixture of products.

Lactam of *cis*-2-Aminomethylcyclohexanecarboxylic acid—Preliminary experiments established that N-benzyl-*cis*-hexahydrophthalimide was unaffected by Raney nickel and hydrogen in cyclohexane at 200–220°.

Accordingly, the tetrahydrophthalimide (K. and K. Co.) 35 g., was submitted to the hydrogenolysis conditions. The solution was filtered, concentrated, and distilled in a small Claisen flask to give 10.9 g. of material, b.p. 135° (1.25 mm.), which crystallized in the receiver. Recrystallization from hexane gave 10.25 g. of material, m.p. 85°.

Anal. Calcd. for $C_8H_{13}ON$: C, 69.0; H, 9.4. Found: C, 65.0; H, 7.8.

This indicated a possible imide impurity. Therefore 7.3 g. (52.5 mmoles) was kept for 19 hours at 35° with 0.50 g. (12.5 mmoles) of sodium hydroxide in 20 ml. of water. The solution was extracted 5 times with 20-ml. portions of chloroform which were dried and evaporated. The residue on crystallization from 20 ml. of hexane gave 3.0 g. of handsome crystals, m.p. 77.0–78.0°.

Anal. Found: C, 69.0; H, 9.3.

Attempted Preparations of Lactam of *cis*-3-Aminomethylcyclohexanecarboxylic Acid.—Ruthenium dioxide in dioxane with hydrogen failed to effect hydrogenolysis of 1,3-cyclohexanedicarboximide. Partial reduction using lithium aluminum hydride in tetrahydrofuran also failed to give the lactam. Raney nickel in cyclohexane with hydrogen gave an ill-defined mixture of products.

Nickel-on-charcoal in dioxane with hydrogen effected partial hydrogenolysis of this imide. Attempts to isolate the lactam by crystallization or distillation failed to separate it from unreacted imide. However, destruction of the latter by a limited amount of alkali might be successful.

***m*-Cresyloxycarbonyl Chloride.**—The reaction of *m*-cresol with phosgene and dimethylaniline in benzene gave *m*-cresyloxycarbonyl chloride,[48] b.p. 96° (8 mm.).

Anal. Calcd. for $C_8H_7O_2Cl$: active Cl^-, 20.8. Found: Cl^-, 20.8, 20.6.

Hydrogenation of 3-Aminophenol.—3-Aminophenol, recrystallized from ethyl acetate, was hydrogenated in water over ruthenium-on-charcoal. Distillation gave a 25.5% yield of mixed 3-aminocyclohexanols, b.p. 115° (0.5 mm.). Treatment with toluenesulfonic acid gave a stereochemically impure salt, m.p. 150.0–152.2°, even after several recrystallizations. Distillations of the free bases in a spinning band column at 0.2 mm. failed to effect separation, as shown also by impure salt formation.

Hydrogenation of N-Acetyl-3-aminophenol. I. Over Ruthenium-on-Charcoal.—N-Acetyl-3-aminophenol, 500 g., was hydrogenated in ethanol over ruthenium dioxide. The catalyst was filtered, the solvent was evaporated, and the residue was crystallized from 500 ml. of ethyl acetate, m.p. 100–102°. Several recrystallizations from ethyl acetate failed to raise the melting point. It then was crystallized twice from 250 ml of acetonitrile to give hard crystals looking unlike previous crops. These were recrystallized finally from ethyl acetate to give superb crystals, m.p. 118.0–118.5°, 65.8 g.

II. **Over Platinum.**—In an Adams hydrogenation apparatus were placed 40 g. of N-acetyl-3-aminophenol, 150 ml. of absolute ethanol and 0.70 g. of platinum oxide. Warming was performed by an infrared lamp and hydrogenation was allowed to proceed overnight during which 0.3 mole (37.7%) was absorbed. Although this was insufficient, the solution was worked up. The catalyst was filtered, the ethanol was removed at the aspirator, and the residue was crystallized from 75 ml. of ethyl acetate. Recrystallization from 180 ml. of ethyl acetate gave a first crop: 11.7 g., 28.2%, m.p. 118.0–121.0°. A second crop, 6.5 g., melted at 107.0–110.5°.

Hydrotosylate of *cis*-3-Aminocyclohexanol.—A mixture of 91.7 g. of *cis*-3-acetylaminocycylohexanol, 112.8 g. of toluenesulfonic acid monohydrate and 97.8 ml. of water was heated under reflux in an oil-bath at 130° for 21 hours. The mixture was cooled somewhat, the water was pumped off under aspirator pressure, and the residue was poured into 2.5 l. of acetone. The product crystallized well; 107.2 g. (64.0%), m.p. 155.5–156.5°.

Anal. Calcd. for $C_{13}H_{21}NSO_4$: C, 54.4; H, 7.4; N, 4.9. Found: C, 54.1; H, 7.4; N, 4.8.

***m*-Cresyloxycarbonyl Derivative of *cis*-3-Aminocyclohexanol.**—A mixture of 2.5 g. of *cis*-3-aminocyclohexanol hydrotosylate, 1.47 g. of *m*-cresyloxycarbonyl chloride, 3.0 g. of MgO and 30 ml. of chloroform was stirred magnetically for 3 days. The solid mush was treated with 30 ml. of 3 *N* HCl and chloroform. The chloroform layer was dried and evaporated and the residue was crystallized from 100 ml. of cyclohexane, giving 1.91 g. (88%) of material, m.p. 133.0–137.0°.

Anal. Calcd. for $C_{14}H_{19}O_3N$: C, 67.2; H, 7.3; N, 5.7. Found: C, 67.5; H, 7.4; N, 5.3.

A similar experiment performed under Schotten–Baumann conditions gave a 72% yield, m.p. 135.5–137.5°.

Bicyclic Urethan of *cis*-3-Aminocyclohexanol.—N-*m*-Cresyloxycarbonyl-*cis*-3-aminocyclohexanol, 34.0 g., 34

(47) E. Ferber and H. Bendix, *Ber.*, **72B**, 839 (1939).

(48) L. C. Raiford and G. O. Inman, THIS JOURNAL, **56**, 1586 (1934).

ml. of *m*-cresol, and 0.68 g. of litharge were heated under a reflux condenser at 150° in an oil-bath for 1 hour. The mixture was rinsed into a separatory funnel with 50 ml. of water and 125 ml. of ether. The water layer was separated and the organic layer was extracted seven times with 50-ml. portions of water. The water layers were filtered and evaporated to dryness on the steam-bath under aspirator vacuum. This gave 17.01 g. of crude solid. Sublimation provided 14.31 g. of hygroscopic white crystals, m.p. 151–152°.

Anal. Calcd. for $C_7H_{11}O_2N$: C, 59.6; H, 7.9; N, 9.9. Found: C, 59.4; H, 7.6; N, 9.8.

Hydrogenation of 4-Aminophenol.—4-Aminophenol, 2 kg., was hydrogenated in water solution over ruthenium-on-charcoal. The catalyst was filtered and the filtrate distilled. Material, b.p. 90–108° (0.5 mm.), was taken in two arbitrary fractions, 370 g. and 188 g. Fraction 1, 350 g., was acetylated with 315 g. of acetic anhydride in 1.8 liters of chloroform. The solvents were removed at 1 mm. Crystallization from methyl ethyl ketone gave material, mostly melting 133–135°, but with appreciable undissolved solid. Recrystallization from ethyl acetate and then chloroform gave 164 g. of white crystals, m.p. 135.5–137°, with very slight speckles observable in the melt. A small, pure sample obtained by extraction of the crystals with insufficient ethyl acetate and recrystallized from chloroform, melted at 135.5–135.9° to a perfectly clear melt.

Hydrotosylate of *cis*-4-Aminocyclohexanol.—The hydrolysis was carried out exactly as described for the 3-isomer. The salt, obtained in 73.4% yield, melted at 197.5–198.5°.

Anal. Calcd. for $C_{13}H_{21}NSO_4$: C, 54.4; H, 7.4. Found: C, 53.9; H, 7.2.

Crystalline *m*-Cresyloxycarbonyl Derivative of *cis*-4-Aminocyclohexanol.—A mixture of 5.0 g. of *cis*-4-aminocyclohexanol hydrotosylate, 6.0 g. of MgO, 2.94 g. of *m*-cresyloxycarbonyl chloride, and 70 ml. of chloroform was magnetically stirred for 3 days at room temperature. To it were added 30 ml. of 3 *N* HCl and more chloroform. The precipitate was filtered and washed with a little 12 *N* HCl and chloroform, only a few particles remaining undissolved. The water layer was separated and extracted with chloroform. The organic layers were dried and evaporated. Addition of cyclohexane to the residue gave an oil. A little acetone was added, the flask was scratched and left at room temperature. The crystals which formed in one day were filtered and washed with cyclohexane, m.p. 75.5–77.5°.

Anal. Calcd. for $C_{14}H_{19}O_3N$: C, 67.4; H, 7.7; N, 5.6. Found: C, 67.5; H, 7.6; N, 5.6.

Bicyclic Urethan from *cis*-4-Aminocyclohexanol.—As noted above, a crystalline *m*-cresyloxycarbonyl derivative of *cis*-4-aminocyclohexanol was obtained only in modest yield. Accordingly, to a solution of 1.44 g. of hydrotosylate of the aminoalcohol and 1.50 g. of potassium carbonate in 25 ml. of water was added with stirring a solution of 1.68 g. of *m*-cresyloxycarbonyl chloride in 15 ml. of acetone. After 40 minutes the mixture was extracted twice with 50-ml. portions of chloroform, the organic layers were dried, and the solvents were removed. From here the procedure was exactly that used to prepare the 1,3-isomer above. The crude product, 0.13 g., gave on sublimation 0.12 g. (15%) of white crystals, completely water-soluble, m.p. 154.0–156.0°.

Anal. Calcd. for $C_7H_{11}O_2N$: C, 59.6; H, 7.9; N, 9.9. Found: C, 59.4; H, 7.6; N, 10.0.

Several modifications of the cyclization procedure, including dilution with *o*-dichlorobenzene, gave no significant improvement in yield. Phenylthiocarbonyl chloride gave inconclusive results.

Hydrogenation of N-Acetyl-4-aminophenol.—N-Acetyl-4-aminophenol, Eastman Kodak Co., 500 g., was hydrogenated in absolute ethanol over ruthenium-on-charcoal. The catalyst was filtered. The filtrate was concentrated and seeded. It crystallized slowly. Filtration and draining overnight on a sintered glass funnel gave 192 g. of crystals. Recrystallization from 250 ml. of ethanol and 750 ml. of ethyl acetate gave, in two crops, 124.5 g. (23.9%) of *trans*-N-acetyl-4-aminocyclohexanol, m.p. 160.0–163.5°.

Hydrotosylate of *trans*-4-Aminocyclohexanol was prepared exactly as described for the 3-isomer in 80.7% yield, m.p. 243.5–245.0°.

Anal. Calcd. for $C_{13}H_{21}O_4NS$: C, 54.3; H, 7.4. Found: C, 54.4; H, 7.5.

***m*-Cresyloxycarbonyl Derivative of *trans*-4-Aminocyclohexanol** was prepared exactly as described for the 3-isomer, in 49% yield, m.p. 176–177° when immersed in a bath at 170°, heating rate 2°/min., soon becomes opaque again.

Anal. Calcd. for $C_{14}H_{19}O_3N$: C, 67.2; H, 7.3; N, 5.7. Found: C, 67.4; H, 7.7; N, 5.6.

Heating this substance at 200° for 15 minutes in the presence of a little litharge gave a white polymer, m.p. 400°, η_{inh} (sulfuric) 0.08.

Directly from 4-Aminocyclohexanol.—4-Aminocyclohexanol, 230 g., b.p. 100–103° (1.2 mm.), was prepared as before. It was fractionally distilled through a spinning band column, pot temperature 150°, 20 mm. pressure, cooling water at 50° to prevent crystallization. A forerun, 15 g., was discarded. Then 166.5 g., b.p. 132.0–134.9° (20 mm.), was taken in 3 fractions, and lastly 20.7 g., b.p. 135–145°. The toluenesulfonic acid salts of the various fractions were *cis-trans* mixtures and melted over broad ranges. Hence the isomers cannot be separated in this way.

The mixture of b.p. 132–135°, 146.5 g., was acylated with 230 g. of *m*-cresyloxycarbonyl chloride, using 1.5 l. of water, 1.5 l. of acetone and 260 g. of K_2CO_3. A white solid formed. Acetone was removed over the weekend under an airjet, leaving a white tar. Addition of 500 ml. of methylene chloride caused this to crystallize. It was filtered and rinsed with 1 l. of 1:1 water–methylene chloride to give 174.7 g. of white crystals, m.p. 174° (hot bar) with melting and resolidification. A mixed melting point with N-*trans*-*m*-cresyloxycarbonyl-4-aminocyclohexanol was undepressed.

The methylene chloride filtrates were evaporated and heated with litharge as above. Working up gave only 1.37 g. of crude product, which on sublimation at 120° (0.3 mm.) gave 0.74 g. pure bicyclic urethan.

3-Hydroxypiperidine.—Hydrogenation of 100 g. of 3-hydroxypyridine in water solution over ruthenium dioxide[49] gave 87.2 g. (82.0%) of material, b.p. 104–107° (14 mm.), m.p. 59.0–62° (lit. b.p. 113°[50–52] (26 mm.), m.p. 61–63°).

***m*-Cresyloxycarbonyl Derivative of 3-Hydroxypiperidine.**—To a solution of 4.75 g. of 3-hydroxypiperidine and 4.0 g. of triethylamine in 75 ml. of methylene chloride was added with stirring 8.0 g. of *m*-cresyloxycarbonyl chloride in 25 ml. of methylene chloride. After 30 minutes the solvent was evaporated and the residue was dissolved in 150 ml. of ether. The solution was washed with 1 *N* HCl and water, dried and evaporated. Addition of cyclohexane containing a little benzene to the residue caused crystallization. The product weighed 6.81 g. (61.6%), m.p. 62.0–64.0°.

Anal. Calcd. for $C_{13}H_{17}O_3N$: C, 66.3; H, 7.0; N, 5.5. Found: C, 66.4; H, 7.3; N, 6.0.

Attempted Preparation of Bicyclic Urethan of 3-Hydroxypiperidine.—Several experiments involving heating *m*-cresyloxycarbonyl-3-hydroxypiperidine with litharge, then working up with ether and water and evaporating the water, gave no product at all. Direct distillation from ester interchange catalysts showed that Sb_2O_3 was ineffective, permitting unchanged material to distil (b.p. 191° at 0.6 mm.). Potassium carbonate gave considerable decomposition. Litharge did likewise, but a little product was obtained.

Ten grams of the cresyloxycarbonyl derivative and 0.02 g. of litharge were heated with an oil-bath at 0.8 mm. At 220° cresol distilled, b.p. to 110°, 3.54 g. The rest was heated with a flame to give 0.92 g. of mobile orange liquid; then decomposition became severe.

Anal. Calcd. for $C_6H_9O_2N$: N, 11.0. Found: N, 2.9.

Occurrence of decomposition rather than polymerization, in contrast to the 4-isomer (see below), recalls the decomposition of 2-oxazolidone under similar circumstances.[2]

4-Hydroxypiperidine.—Hydrogenation of 100 g. of 4-hydroxypyridine in water over ruthenium[49] gave, on distillation, 74.7 g. of 4-hydroxypiperidine,[53] b.p. 88° (0.5 mm.), m.p. 85.5–88.0°.

N-*m*-Cresyloxycarbonyl Derivative of 4-Hydroxypiperidine was prepared from *m*-cresyloxycarbonyl chloride and

(49) Dr. J. R. Schaefgen, unpublished work, these laboratories.

(50) C. F. Koelsch and J. J. Carney, THIS JOURNAL, **72**, 2285 (1950).

(51) C. H. Keng, *C. A.*, **44**, 3993 (1950).

(52) J. H. Biel, H. L. Friedman, H. A. Leiser and E. P. Sprengeler, THIS JOURNAL, **74**, 1485 (1952).

(53) B. Emmert and W. Dorn, *Ber.*, **48**, 688, 957 (1915).

4-hydroxypiperidine in methylene chloride, using triethylamine as the acid acceptor. The crude product recrystallized well from benzene–hexane, m.p. 84–86° in 67.3% yield.

Anal. Calcd. for $C_{13}H_{17}O_3N$: N, 5.5. Found: N, 6.0.

Attempted Preparation of Bicyclic Urethan of 4-Hydroxypiperidine.—The *m*-cresyloxycarbonyl derivative of 4-hydroxypiperidine underwent loss of *m*-cresol less readily than the 3-isomer. Thus distilling 10.0 g. from 0.02 g. of litharge at 220° gave back 8.82 g. of starting material, b.p. 210–212° (0.8 mm.).

Attempts to polymerize this monomer directly gave poor results as did attempts to copolymerize it with the corresponding derivatives of 3-hydroxypiperidine or *trans*-4-aminocyclohexanol.

Cyclohexane-1,3- and 1,4-Diols.—Hydrogenation of resorcinol in ethanol over ruthenium gave a little cyclohexanol and the 1,3-diol, b.p. 107° (1.4 mm.) −110° (1.0 mm.).[54]

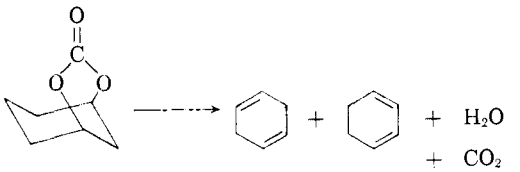
The 1,4-diol was obtained from Halogen Chemicals, Inc.

Cyclohexane-1,3-diol Cyclic Carbonate.—A mixture of 30.0 g. of cyclohexane-1,3-diol, 32.0 g. of diethyl carbonate and 0.20 g of K_2CO_3 was heated slowly under a column to 200°.[55] Ethanol, 20 ml., smelling of some cyclohexadiene, was removed. The residue was cooled and attached to a Claisen distillation assembly. A vacuum of 0.4 mm. was applied and heating was begun. A little volatile material and unreacted diol, b.p. 120°, were discarded. The condenser was replaced by an ice-cooled flask, vacuum was reapplied and the residue was heated slowly to 250°. A white sublimate came over, leaving only a little clear resin. Slight decomposition was occurring, the final pressure being 4.5 mm. The distillation was stopped and benzene was boiled through the apparatus to extract all the sublimate. The extract was filtered through Celite and evaporated. Addition of 80 ml. of ether to the residue caused it to crystallize, giving 8.14 g. of white solid. Sublimation of 3.00 g. of this at 175° (0.5 mm.) gave, after a little sticky presublimate, 2.84 g. of white crystals, m.p. 173.0–174.0°.

Anal. Calcd. for $C_7H_{10}O_3$: C, 59.1; H, 7.1. Found: C, 59.2; H, 6.9.

As catalysts, potassium hydroxide, litharge, tetraisopropyl titanate, aluminum triethoxide and antimony oxide were unsatisfactory. Diphenyl carbonate in place of diethyl carbonate also was poor.

This cyclic carbonate underwent an interesting acid-catalyzed decarboxylation to form a mixture of cyclohexadienes



A mixture of 6.0 g. of cyclic carbonate and 0.25 g. of 2,5-dichlorobenzenesulfonic acid was heated in a small distilling flask in an oil-bath at 200° for 40 minutes. Gas was evolved and distillation occurred slowly, the maximum head temperature being 83°. There was obtained 2.73 g. of distillate (two phases) with the characteristic odor of cyclohexadiene. The lower phase was 0.60 g. of water. The upper layer was dried, treated with 2.0 g. of maleic anhydride in 35 ml. of ether, and kept overnight at room temperature. The solution, which still smelled strongly of diene, was evaporated to a semi-crystalline mass. This was extracted with 30 ml. of 5:1 heptane–benzene, filtered and evaporated under an airjet to give 0.28 g. of white needles, m.p. 146–148° (lit.[56,57] m.p. 147° for the adduct of 1,3-cyclohexadiene with maleic anhydride).

An analogous procedure applied to cyclohexane-1,4-diol gave a 12% yield of impure 1,4-bicyclic carbonate.

Anal. Calcd. for $C_7H_{10}O_3$: C, 59.1; H, 7.1. Found: C, 61.5; H, 9.8.

The infrared spectrum showed strong C=O and OH absorption. Rinsing the impure material with methylene chloride, filtering and evaporating the filtrate gave a *ca.* 50:50 mixture of diol and carbonate.

Ureas from 1,3- and 1,4-Diaminocyclohexane.—A mixture of 16.2 g. of 1,3-diaminocyclohexane, 17.0 g. of diethyl carbonate and 0.2 g. of NaH was heated for 2 hours. Ethanol, 10.5 ml., distilled smoothly. The oily semi-crystalline, water-insoluble residue was rinsed into 100 ml. of acetone, filtered and sublimed at 210° (0.3 mm.). A gas (ethanol) evolved during the sublimation. The cyclic urea, 5.18 g. (26.0%), melted at 323° (lit. m.p. 316°). The modest yield may be due to the presence of some *trans*-diamine which could give only polymer.

cis-1,4-Diaminocyclohexane gave no sublimable or water-soluble material on similar treatment or on reaction with diphenyl carbonate.

Cyclohexane-1,3- and 1,4-dicarboxylic acids were prepared by hydrogenating dimethyliso- or terephthalate in an equal volume of dioxane over ruthenium-on-charcoal. The dioxane was removed with aspirator vacuum and the crude ester was hydrolyzed by boiling with 3× its weight of 36% HCl for 8 hours. The acids solidified and crystallized on cooling.[58–60]

Cyclohexane-1,3-dicarboximide.—To 75 g. of cyclohexane-1,3-dicarboxylic acid was added cautiously 150 ml. of 30% ammonium hydroxide. Water was distilled slowly over 2 hours with a heating mantle, and the residue was distilled rapidly with a free flame, all but a small amount coming over. To the distillate was added 100 ml. of water. The *p*H was 4.7 and 40 ml. of 10% sodium hydroxide was required to bring it to 7.0. A heavy white precipitate which formed was taken up in 100 ml. of chloroform, the water layers were extracted with four 100-ml. portions of chloroform. The organic layers were evaporated and the residue was sublimed at 120° (1 mm.) to give 29.3 g. (52.1%) of imide, m.p. 189.0–191.0°.

Anal. Calcd. for $C_8H_{11}O_2N$: N, 9.1. Found: N, 9.0.

Cyclohexane-1,3-dicarboxylic-N-methylimide.—The reaction was carried out similarly, using 105 g. of acid and 210 ml. of 40% aqueous methylamine. The distillate solidified in the receiver and contained almost no acidic impurities. It was taken up in 225 ml. of chloroform, dried and evaporated. Addition of hexane to the residual oil caused it to crystallize well, and chilling and filtration gave 63.0 g. (72.2%) of glittering plates, m.p. 58.5–59.5°.

Anal. Calcd. for $C_9H_{13}O_2N$: N, 8.4. Found: N, 8.3, 8.3.

Cyclohexane-1,3-dicarboxylic anhydride was prepared by the method of Perkin, crystallized from benzene–hexane, and sublimed at 140° (0.5 mm.). It melted at 167–186°, although it was of good appearance (lit. m.p. 189°).

Anal. Calcd. for $C_8H_{10}O_3$: C, 62.3; H, 6.5. Found: C, 62.0; H, 6.6.

Bicyclic Lactone of 4-Hydroxycyclohexanecarboxylic Acid.—Hydrogenation of *p*-hydroxybenzoic acid in water over ruthenium dioxide, and then distillation of the acid at 190° (15 mm.) gave the crude lactone. Two crystallizations from heptane, then sublimation, gave lactone, m.p. 126–127°.

Bicyclic Lactone of 3-Hydroxycyclohexanecarboxylic Acid.—One attempt to prepare the lactone from the free acid gave a product contaminated with an oily impurity. The latter was not an acid, for treatment with *p*H 7 buffer did not remove it. Accordingly the lactone was prepared by ester interchange.

Hydrogenation of 200 g. of ethyl *m*-hydroxybenzoate (K. and K. Laboratories) over ruthenium dioxide in ethanol gave 165 g. of ethyl 3-hydroxycyclohexanecarboxylate, b.p. 90° (0.50 mm.). Heating 65.5 g. of this ester with 0.10 g. of litharge at 190° for 1 hour caused 12 ml. of ethanol to distil. Pressure was reduced to 10 mm. and the residue distilled at 129°. Two recrystallizations from ether at −80°, and then sublimation at 100° (0.5 mm.), gave 20.8 g. of hygroscopic white solid, m.p. 126–131°.

Anal. Calcd. for $C_7H_{10}O_2$: C, 66.64; H, 7.99. Found: C, 66.98; H, 7.91.

Polymerizations of bicyclic monomers were carried out as described earlier.[1,2] Cyclic esters, urethans and imides

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(59) P. C. Guha and G. D. Hayra, *J. Indian Inst. Sci.*, **22A**, 263 (1938); *C. A.*, **34**, 2822 (1940).
(60) Dr. S. L. Jung, unpublished work, these laboratories.

were heated at 100–200° for 24 hours with litharge, potassium carbonate, sodium hydride, tetraisopropyl titanate and 2,5-dichlorobenzenesulfonic acid. Lactones and cyclic ureas were heated at 150–260° with water and sodium hydride for a similar period.

Lactam VI polymerized so quickly when heated to 200° that melting could not be completed before the polymer congealed. Attempts to moderate the reaction with milder catalysts (see below) or by conducting it in solution in ethyl benzoate, γ-butyrolactone, pyrrolidone or 5,5-dimethylpyrrolidone,[1] gave no improvement in yield or molecular weight. Lactam V polymerized at a much slower rate and addition of N-acetylcaprolactam was beneficial. Lactone IV polymerized at about the same rate, confirming earlier work.[6,7] Lactone XI polymerized slowly to give a low molecular weight, solvent-sensitive polymer. The polyurethan obtained from XII was also sensitive to solvent and of low molecular weight.

Because the reaction of VI with sodium hydride proceeded too rapidly for convenient control, a search was made for other catalysts. The following were ineffective (at 200° for 24 hours): water, ε-aminocaproic acid, sodium or potassium carbonate, sodium acetate, boric acid, sodium phosphite, litharge, antimony trioxide, tetraisopropyl titanate, γ-butyrolactone, toluenesulfonic acid and sodium cyanide. All salts were tested with and without a trace of water. Phosphoric acid gave a very small yield of polymer. At the boiling point of the lactam, sodium phenoxide and carbonate were still ineffective.

Poly-3-cyclohexanecarboxamide was soluble in *m*-cresol, sulfuric acid, trifluoroacetic acid, 90 and 99% formic acids, 60% trichloroethane–40% formic acid and 60% chloroform–40% formic acid. The 4-isomer dissolved in sulfuric acid, 99% formic acid, and in the mixtures of the latter with chloroform and trichloroethane. It was insoluble in *m*-cresol, trifluoroacetic acid and 90% formic acid.

Both polymers depolymerized to the corresponding lactams when heated with a flame, the 1,3-isomer at lower temperatures.

Because of the possibility of isomerization during polymerization, these polymers may be mixtures of *cis* and *trans* forms.

Chelates.—A relationship between ease of formation of chelate compounds and of bicyclic organic compounds has been noted and discussed.[61–63] In agreement with this concept, the feasibility of forming cyclic and bicyclic ureas from diamines could be assessed by seeing whether or not they formed chelates with metal ions.

The diamine was added to an aqueous solution of cupric acetate. The appearance of an intense violet color was taken as an indication of chelate formation. The following gave positive tests: ethylenediamine, trimethylenediamine, *cis*-1,3-diaminocyclohexane, *cis*- and *trans*-1,4-diaminocyclohexane and 1,8-diamino-*p*-menthane gave negative tests. This order is in good accord with the observed tendencies of these diamines to form cyclic ureas. This test should also apply to aminocyclohexanols.

For the best results a metal atom should have the same stereochemistry as the carbon atom to which it will correspond. However, we have used copper (square planar) to correspond to carbonyl carbon (trigonal planar) because of easily observed color changes on chelation.

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

Hydrolysis Rates and Mechanisms of Cyclic Monomers

BY H. K. HALL, JR., M. K. BRANDT AND R. M. MASON

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The rates of hydrolysis of a number of imides, N-acyllactams and lactones were determined. The data were combined with information in the literature and compared with the polymerizability of the cyclic compounds. No correlation was observed, hence hydrolysis rates do not measure ring strain. The slow step in the hydrolysis is the addition of OH^- to the ring, leaving the ring unbroken. The enhanced reactivities of lactones over esters was ascribed to repulsion of the lone pair electrons on oxygen in the latter toward the hydroxyl ion. This postulate uses the transition state proposed by Ballard and Bamford, which is also consistent with substituent effects in the 5-membered rings. The 6-membered compounds showed the usual rate depression caused by 1,3- interaction with methyl substituents.

Carothers[1] suggested that polymerizability and rates of hydrolysis of cyclic monomers should run parallel.[1] It is the purpose of this article to examine this suggestion more closely.

The results of the investigation are given in Table I and are summarized in Table II.

Relationship of Hydrolysis Rate to Polymerizability.—Rings of extremely high reactivity to alkali relative to the acyclic derivative are prone to polymerize. These include ethylene oxalate,[1] δ-valerolactone,[1] propiolactam,[2] 2,5-piperazinedione,[3] lactide[4] and glycolide.[4] To this extent Carothers' proposal is valid.

Other rings show no correlation with polymerizability. For example, 2-piperidone hydrolyzes faster than 2-pyrrolidone, yet the polymerizabilities are markedly in the reverse order.[5] Propiolactone polymerizes readily and γ-butyrolactone does not, yet the two lactones hydrolyze at comparable rates.[6] The suggestion of Carothers is therefore not generally valid.

Polymerizability of a cyclic compound is an indication of strain in the ring[7] and since the hydrolysis rate is not determined by strain in the ring, it follows that the ring is not broken in the rate-determining step; the latter must consist of addition of OH^- to the ring, in agreement with Bender's results for open-chain compounds.[7c]

Reactivity of Cyclic Compounds Relative to Acyclics.—Table III makes clear that only lactones (and possibly cyclic carbonates)[8] exhibit a large

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(7) (a) G. E. Wheland, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 366; (b) F. S. Dainton and K. J. Ivin, *Quart. Revs.*, **12**, 82 (1958); (c) M. L. Bender, THIS JOURNAL, **73**, 1626 (1951), and later papers.
(8) Sh. Sarel and A. Pothoryles, *Compt. rend.*, **245**, 2321 (1957).