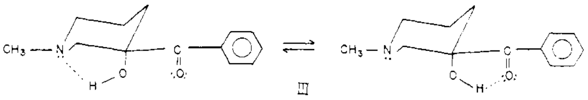
cm.$^{-1}$, nearly four times as great a shift as that for the intramolecular hydrogen bond in the 3-piperidinols. Molecular models suggest reasons why the O—H . . . N hydrogen bond may be unusually weak in 3-piperidinols. Some distortion of the ring would be necessary for the hydroxyl hydrogen to come within effective bonding distance of the nitrogen atom. Moreover, the hydrogen bond in 3-piperidinols must be strongly angular, a factor which is known to lead to weakening of hydrogen bonds.[3,9]

Finally, the compound *dl*-1-methyl-3-benzoyl-3-piperidinol (III) will be considered. This compound, like its 4-substituted isomer discussed above has a strong broad absorption band at 3455 cm.$^{-1}$, attributable to intramolecular hydrogen bonding to carbonyl oxygen. However, unlike the 4-substituted compound and 1-benzoylcyclohexanol, compound III has a weak shoulder near 3350 cm.$^{-1}$ but no free hydroxyl band near 3620 cm.$^{-1}$.



III

It therefore seems probable that molecules with hydrogen bonds both to carbonyl oxygen and to nitrogen are present in solutions of *dl*-1-methyl-3-benzoyl-3-piperidinol. The O—H . . . N absorption band would be expected to be shifted to lower frequency than in the other 3-piperidinols, because of the acid-strengthening effect of the benzoyl group on the hydroxyl hydrogen. This absorption band may lie at about the same frequency as the O—H . . . O band, or may cause the shoulder at 3350 cm.$^{-1}$.[10] Hydrogen bonding interaction between hydroxyl and nitrogen in III previously was predicted[7] from optical rotatory dispersion studies. Compound III, as the pure *d*-isomer, shows no inversion in the sign of the Cotton effect in going from aqueous acidic solution to octane solution, while the analogous *l*-α-halogenated ketone (III with chlorine in place of hydroxyl) shows a reversal in sign of the Cotton effect in going from one solvent to another.

Acknowledgment.—The authors wish to thank Parke–Davis and Co. for partial support of this research.

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[9] L. Hunter, in W. Klyne, edit., "Progress in Stereochemistry," Vol. I, Academic Press, Inc., New York, N. Y., p. 224.

[10] The shoulder might also be the first overtone of the carbonyl stretching vibration at 1665 cm.$^{-1}$.

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

Synthesis and Polymerization of Atom-bridged Bicyclic Lactams

BY H. K. HALL, JR.

RECEIVED JULY 20, 1959

The polymerizabilities of a variety of atom-bridged bicyclic lactams were studied and compared with expectation based on conformational analysis. Agreement was good, supporting the idea that H–H crowding is the major factor causing polymerization of these compounds. An attempt to prepare a lactam possessing a nitrogen atom at the bridgehead, but free of H–H crowding, namely 1-azabicyclo[3:3:1]nonan-2-one (XXII), led only to the corresponding polyamide. This is the first case in which polymer is favored over monomer in the bicyclo[3:3:1]nonane system and emphasizes the reluctance of the amide link to deviate from coplanarity.

Introduction

Polymerization is a powerful method for detecting conformational strains in cyclic compounds.[1] The merit of this method is that it provides direct experimental measurement of the equilibrium between cyclic monomer and linear polymer, and does not require an indirect assessment of various contributions to the strain.

In earlier work the polymerizabilities of a variety of monocyclic and bicyclic compounds were examined. The present article expands the study to other atom-bridged bicyclic lactams.

Synthesis of Lactams.—Most of the required lactams were prepared by Beckmann rearrangements from bicyclic ketones which had been prepared by previous investigators. The rearrangements were carried out by the addition of benzenesulfonyl chloride to a solution or suspension of the oxime in concentrated alkali.[2] The pertinent details are given in the Experimental section. The ketones and lactams are listed for the most part in Table I.

A few remarks are pertinent. The rearrangements of bicycloheptanone and bicyclooctanone oximes (and the polymerization of the resulting lactams) have been described in three Swiss patents.[3] We have been unable to duplicate these claims.

2-Azabicyclo[3:2:1]octan-3-one (II) was the only lactam not obtained in apparently stereochemically pure form. Bicycloheptanone oxime occurs as an oily mixture of *syn* and *anti* isomers which on rearrangement gave a mixture of isomeric lactams which we were unable to separate. There were indications of other isomers in the preparation of IV and VI (variable m.p. of oxime, only partial crystallization of lactam), but in these cases a pure crystalline isomer could be obtained.[2]

The lactam structures given in Table I are based on the assumption that the migrating group is that which forms the stablest carbonium ion. In nortricyclanone oxime, the cyclopropane ring is assumed to migrate.[4]

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[1] H. K. Hall, Jr., THIS JOURNAL, **80**, 6412 (1958).

[2] M. Gates and S. P. Malchick, *ibid.*, **79**, 5546 (1957).

[3] Swiss Patents 270,546 (1951); 280,367 (1952) and 287,863 (1953) to Inventa AG, Lucerne.

[4] W. D. Burrows and R. H. Eastman, THIS JOURNAL, **79**, 3756 (1957).

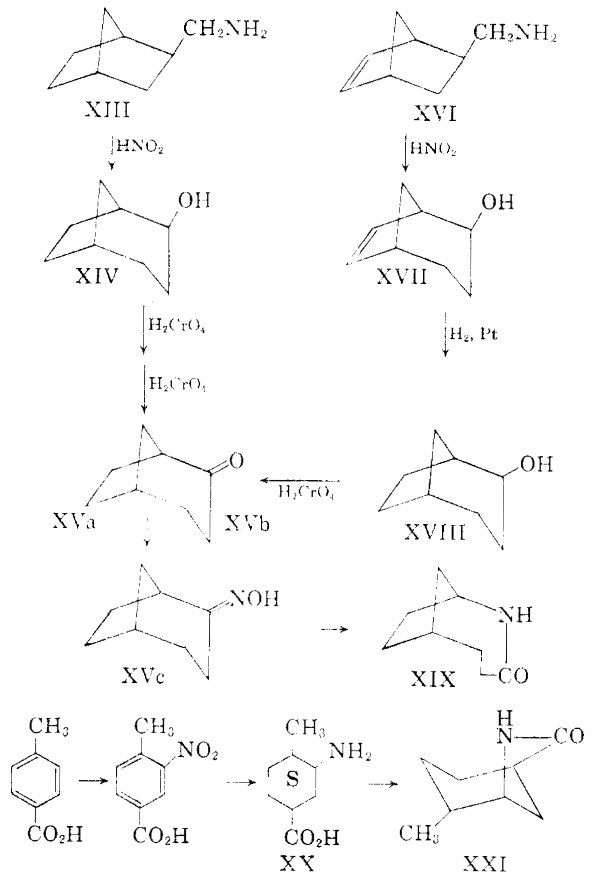
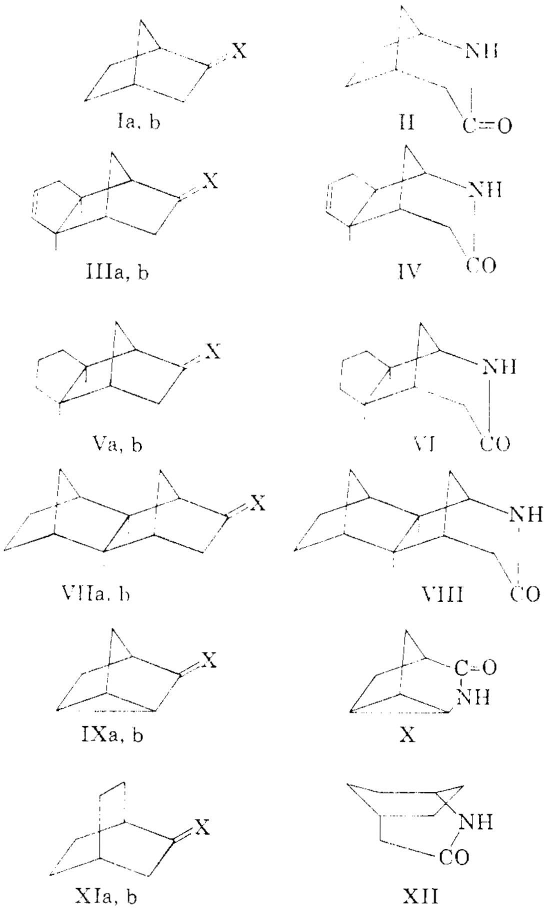


Fig. 1.—Reaction sequence.

Table I

Ketones, Oximes and Lactams: a, X = O; b, X = NOH



Brown and van Gulick[5] observed the base-catalyzed formation of a lactam from an olefinic amide. This prompted us to attempt the cyclization of 3-cyclohexene-carboxamide and of bicyclohept-2-ene-5-carboxamide. However, neither bridged lactam nor polymer formed in either case.

Polymerizations of the lactams were carried out as described in earlier articles, using either water–phosphoric acid or sodium hydride–acetic anhydride catalysts at various temperatures.[1]

Correlation of Strains with Polymerizability.—Table II gives the three types of strain,[1] namely, angle, H–H interaction and inhibition of the N–CO resonance, estimated from models. The atom-bridged lactams studied in the present and previous work are given.

Each lactam which can relieve strain by undergoing polymerization does so. Conversely, where strain is not present, or cannot be relieved by conversion into polymer, no such conversion is observed. The conformational formulas, therefore, adequately predict the behavior of these bridged lactams, giving further support to the statement in the introduction.

Although Hall[6] was unable to confirm an earlier report[7] that 2-piperidone could be polymerized, Yoda and Miyake[8] have recently shown that this polymer can indeed be prepared, although in only moderate molecular weight. Scrupulously dry monomer and long reaction times appear to be essential to the success of this transformation. In the present paper, therefore, failure to polymerize various bridged monomers can only be taken to indicate that these monomers polymerize, if at all, with far less facility than 2-pyrrolidone or caprolactam.

Substituents on an acyclic chain are well known to favor cyclization. The literature is less clear on whether substitution on a monocyclic compound will favor further cyclization to a bridge bicyclic compound. In the single case examined in the present work, 4-methyl-6-azabicyclo[3:2:1]octan-7-one failed to polymerize while the unmethylated compound polymerized very readily. More information on this point would be desirable.

Bridgehead Lactams.[9]—Atom bridged lactams of the bicyclo[2:2:2]octane series (two-boat form) with nitrogen at the bridgehead have only recently been prepared.[10,11] It was of interest to see whether a bridgehead lactam of the bicyclo[3:3:1] series (two-chair form) XXII would form readily owing to the absence of non-bonded interactions.

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[5] R. F. Brown and N. M. van Gulick, This Journal., **77**, 1092 (1955).

[6] H. K. Hall, Jr., *ibid.*, **80**, 6404 (1958).

[7] C. E. Barnes, W. R. Nummy and W. O. Ney, Jr., U. S. Patent 2,806,841 (1957).

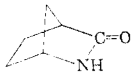
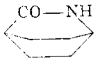
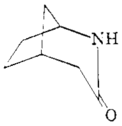
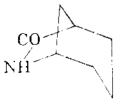
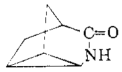
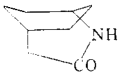
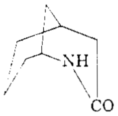
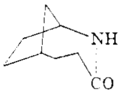
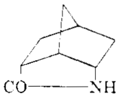
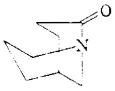
[8] N. Yoda and A. Miyake, *J. Polymer Sci.*, in press.

[9] F. S. Fawcett, *Chem. Rev.*, **47**, 258 (1950).

[10] L. N. Yakhontov and M. V. Rubtsov, *J. Gen. Chem. U.S.S.R.* (*Eng. trans.*), **27**, 83 (1957).

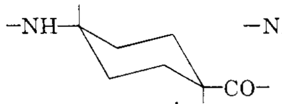
[11] H. Pracejus, *Chem. Ber.*, **92**, 988 (1959).

TABLE II
STRAIN AND POLYMERIZABILITIES OF ATOM-BRIDGED BICYCLIC LACTAMS

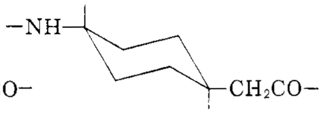
Lactam structural formula	Name	Estimated strain[a]			Polymerizability
		Angle	H-H	N-CO	
	2-Azabicyclo[2:2:1]heptan-3-one	+	$+^b$	+	Predict +
	2-Azabicyclo[2:2:2]octan-3-one	0	+	0	+
	2-Azabicyclo[3:2:1]octan-3-one (II)	Small	$+^b$	0	−
	6-Azabicyclo[3:2:1]octan-7-one	+	0	+	+
	3-Azatricyclo[3:2:1:$0^{4,6}$]octan-2-one (X)	$++^{b,c}$	$+^b$	0	−
	2-Azabicyclo[3:2:2]nonan-3-one (XII)	0	+	0	+
	2-Azabicyclo[3:3:1]nonan-3-one	0	0	0	Predict −
	2-Azabicyclo[4:2:1]nonan-3-one (XIX)	0	$+^d$	0	+
	6-Azatricyclo[3:2:1:$1^{3,8}$]nonan-7-one	+	$+^b$	+	Predict +
	1-Azabicyclo[3:3:1]nonan-2-one (XXII)	0	0	+	+

[a] Stuart–Briegleb–Lapine models were used. [b] Strain not relieved in polymer. [c] Flexible bonds used to make model. [d] Strain partially relieved in polymer.

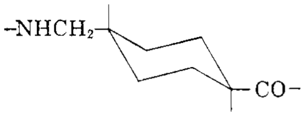
TABLE III
POLYMER MELTING POINTS



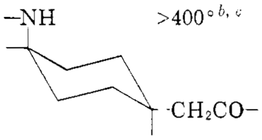
>400°[a, f]



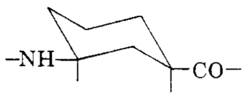
>400°[b, c]



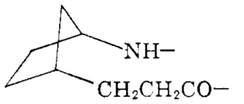
350°[d]



212°[e]



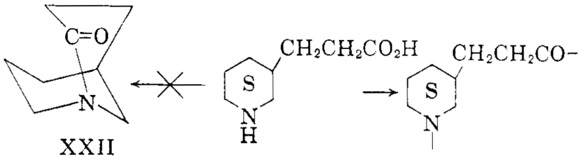
>400°[a]



222°[e]

[a] H. K. Hall, Jr., THIS JOURNAL, **81**, 6412 (1959). [b] A. J. Hill, *Fibers*, **18**, 402 (1957). [c] British Patent 782,441 (1957). [d] V. Sziraky, unpublished work, these laboratories. [e] Present work. [f] Isomerization to the stable *trans*-polymer is assumed to have taken place under the influence of the sodium hydride catalyst.

3-(β-Piperidyl)-propionic acid when heated under vacuum gave exclusively polyamide and no bridged lactam was found. Therefore the preference for N–CO coplanarity renders the monomer sufficiently unstable to polymerize, a unique result in the bicyclo[3:3:1]nonane series.[1]



XXII

Polymer Structures and Melting Points.—Table III summarizes the available information. It appears that incorporation of the 1,4- and 1,3-diequatorial chair forms of cyclohexane in the chain causes the polymer to have a high melting point, rather like *m*- or *p*-disubstituted benzene rings. Also, as usual, additional methylene groups lower the melting point.

Acknowledgments.—I am deeply indebted to the following individuals and their associates: to Mr.

I. D. Plank for the microanalyses, Mr. H. E. Cupery for the hydrogenation, Mr. H. Thielke for the vapor phase chromatograms, to Mr. George Elechko for excellent technical assistance, and to Dr. P. W. Morgan for unfailing encouragement.

Experimental

Melting points and boiling points are uncorrected.

Ketones.—Bicyclo[2:2:1]heptanone-2 (norcamphor) (Ia) was prepared[12] *via* the addition of vinyl acetate to cyclopentadiene, hydrogenation, and hydrolysis of the ester to give a mixture of norborneols, m.p. 138.5–140.0°.

The oxidation was carried out according to Vosburgh's procedure, which was also used for the preparation of the other ketones. His directions are as quoted: To a solution of 235 g. of potassium dichromate and 109 ml. of 96% sulfuric acid in 1.2 l. of water was added over 1.5–3 hours with vigorous stirring 124 g. of norborneol. The temperature was not allowed to exceed 50°. After the addition was complete, the mixture was allowed to cool to room temperature with continued stirring over 0.5–1.5 hours. It was extracted three times with 600-ml. portions of ether, which were combined and washed three times with 400-ml. portions of 5% sodium hydroxide solution, dried and evaporated. Removal of the final traces of ether at aspirator pressure left a clear glass which soon crystallized, m.p. 88–89°. Sublimation at 100° gave 97 g. (79.5%) of norcamphor, m.p. 92–93° (lit. m.p. 91–92°,[13a] 93–94°.[13b]

This oxidation procedure was superior to alternative ones using acetic acid. In the case of alcohols with two or more fused rings, the addition of minor amounts of acetone was beneficial in facilitating mixing.

Bicyclo[2:2:2]octanone-2 (VIa).—The addition of vinyl acetate to 1,3-cyclohexadiene, hydrogenation, and hydrolysis provided bicyclo[2:2:2]octanol-2, m.p. 213.0–213.5° (lit.[14] m.p. 216–217°). Oxidation provided the ketone in 88.6% yield, m.p. 173–177° (lit. m.p. 176°,[14] 178–179°).[15]

Bicyclo[3:2:1]octanone-2 (XVa).—Bicyclo[2:2:1]heptyl-2-methylamine (XIII), b.p. 71° (19 mm.) –80° (15 mm.) (lit.[17], b.p. 68–71° (12 mm.)), $n^{25}\text{D}$ 1.4869 (lit.[17] $n^{25}\text{D}$ 1.4866–1.4872), was prepared as described by Alder and Windemuth.[16] A crystalline hydrotosylate, m.p. 162–165°, was prepared in ethyl acetate solution and submitted to the Demjanov rearrangement as described by these authors.[16] A final crystallization of the product from hexane at –80° gave a 56.2% yield of bicyclo[3:2:1]octanol-2 (XIV), m.p. 179–180° (lit.[16] m.p. 183°). The infrared spectrum showed the required groups to be present, but the compound appeared to be inhomogeneous.

Oxidation provided ketone XVa, m.p. 138.5–139.0° (lit.[16] m.p. 129°), in 76.0% yield.

Although the melting points of alcohol XIV and of ketone XVa correspond roughly with the literature values, this ketone preparation proved on oximation to be much less homogeneous than ketone XVb (see below). Since this work was completed, Alder and co-workers have reinvestigated the Demjanov rearrangement of XIII.[17] They find that employment of a mixture of *endo-* and *exo*-isomers of XIII does indeed lead to XIV seriously contaminated with other alcohols.

Bicyclo[3:2:1]octanone-2 (XVb).—Heating 280 g. (4.24 equivalents) of dicyclopentadiene and 240 g. (4.20 moles) of allylamine at 185° for 20 hours provided 216 g. (41.8%) of amine XVI, b.p. 70–77° (18 mm.), $n^{25}\text{D}$ 1.4958 (lit.[16] b.p. 61–62° (12 mm.)). The amine (213 g., 1.74 moles) was treated with 325 g. (1.71 moles) of *p*-toluenesulfonic acid monohydrate in 2.0 liters of ethyl acetate to give 371.8 g. (73.6%) of finely crystalline hydrotosylate, m.p. 144–146°. This was submitted to the Demjanov rearrangement as before, using a total of 140 g. of sodium nitrite, 124 ml. of acetic acid and 900 ml. of water. The product, worked up as before, was distilled in a spinning band column. A forerun, 10.6 g., b.p. 67–89° (17 mm.), was discarded. The major product XVII, taken in six fractions, 76.1 g. (48.6%), boiled at 89–101° (17 mm.), the latter fractions crystallizing in the receiver. These cuts autoöxidized and became yellow rapidly on keeping, and satisfactory analyses were not obtained.

Anal. Calcd. for $C_8H_{12}O$: O, 12.9. Found (fraction 2): O, 14.2. Found (fraction 5): O, 13.7.

Neutral permanganate solution gave an immediate precipitate of manganese dioxide when treated with this compound.

The unsaturated alcohol, 75.0 g., was dissolved in ethanol and hydrogenated over platinum oxide. After hydrogenation the catalyst was filtered and the solvent was evaporated at 20 mm. from the filtrate to leave a semi-crystalline slurry, 73.5 g. (96.8%). A small portion of this substance was crystallized from ether at –80° to give white crystals of XVIII, m.p. 193.0–193.5°.

Anal. Calcd. for $C_8H_{14}O$: O, 12.68. Found: O, 12.85.

The infrared spectrum showed this material to be homogeneous and free of the above preparation XIV of this alcohol.

The alcohol XVIII, 72.5 g., was oxidized as before and the product was distilled in a spinning band column. After 14.7 g. of colorless liquid, b.p. 82.5–96.0° (23 mm.), had been removed, the distillate began to crystallize. The remaining material was crystallized from 50 ml. of hexane at –80° to give, in two crops, 16.0 g. of white crystals. The mother liquors were distilled at 20 mm. to give an additional 6.0 g. of white solid. Recrystallization of the combined solids from 50 ml. of hexane at –80° gave a first crop of 4.95 g., m.p. 114.5–116.0°, and a second crop of 6.85 g., m.p. 118.0–118.5°, a combined yield of 16.0% of XVb. The infrared spectrum showed this material to be very similar to XVa, but more homogeneous.

Anal. Calcd. for $C_8H_{12}O$: O, 12.88. Found: O, 12.25.

It, therefore, appears that the mixture of alcohols XVIII was not solely a mixture of stereoisomeric alcohols of the formula given, since such a mixture would have given homogeneous ketone.

Nortricyclanone (IXa).—Addition of bicycloheptadiene to formic acid at reflux temperature gave a 62.5% yield of nortricyclyl formate, b.p. 63–67° (12 mm.), $n^{25}\text{D}$ 1.4735 (lit.[18] b.p. 79° (21 mm.), $n^{20}\text{D}$ 1.4758). Sodium-catalyzed methanolysis of this ester, with distillation of methyl formate, gave a 93.1% yield of nortricyclanol, m.p. 103–104° (lit. m.p. 108–109°,[19] 101–102°[18]). Oxidation of the alcohol with sodium dichromate–sulfuric acid[12a] gave a 58.2% yield of nortricyclanone (IXa), b.p. 183–187°. Oxidation using chromic anhydride–acetic acid,[20] with a final purification by crystallization from an equal volume of hexane at –80° gave a 23.9% yield of pure ketone, b.p. 78–79° (24 mm.), $n^{25}\text{D}$ 1.4878.

Anal. Calcd. for C_7H_8O: O, 14.8. Found: O, 14.82.

The 2,4-dinitrophenylhydrazone[21] melted at 184–185° after one crystallization from ethanol (lit.[19] m.p. 188–190°).

4,7-Methano-3a,4,5,6,7,7a-hexahydroindene-5-one (IIIa) was prepared according to Bruson and Riener.[20] It had b.p. 103–105° (9 mm.) (lit. b.p. 130–132° (29 mm.)).

4,7-Methanohexahydroindane-5-one (Va) was prepared as described by Bruson and Riener.[20] It boiled at 109–111° (13 mm.) (lit.[20] b.p. 129–132° (29 mm.)).

1,4,5,8-Bis-endomethano-2-decalone (VIIa) was prepared substantially according to Alder and Rickert.[12b] The alcohols resulting from hydrolysis of the acetate were separated by filtration into a crystalline and a liquid portion in the ratio 1.3:1. Oxidation of solid alcohol, m.p. 65–72° (lit.[12b] m.p. 90–92° for recrystallized material) gave homogeneous ketone, b.p. 85° (0.10 mm.), $n^{25}\text{D}$ 1.5312 (lit.[22]

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[12] (a) W. G. Vosburgh, Thesis, University of Delaware, 1956; (b) K. Alder and H. F. Rickert, *Ann.*, **543**, 1 (1939).

[13] (a) O. Diels and K. Alder, *Ann.*, **470**, 76 (1929); (b) S. V. Hintika and G. Komppa, *Ann. Acad. Sci. Fennicae*, [A] **10**, 1 (1918); *Chem. Zentr.*, **89**, II, 370 (1918).

[14] G. Komppa, *Ber.*, **68B**, 1267 (1935).

[15] O. Diels, K. Alder, E. Petersen and F. Querberitz, *Ann.*, **478**, 137 (1930).

[16] K. Alder and E. Windemuth, *Ber.*, **71B**, 1939, 2404 (1938).

[17] (a) K. Alder, K. Heimbach and R. Reubke, *Chem. Ber.*, **91**, 1516 (1958); (b) K. Alder and R. Reubke, *ibid.*, **91**, 1525 (1958).

[18] L. Schmerling, J. P. Luvisi and R. W. Welch, This Journal, **78**, 2819 (1956).

[19] J. D. Roberts, E. R. Trumbull, Jr., W. Bennett and R. Armstrong, *ibid.*, **72**, 3116 (1950).

[20] H. A. Bruson and T. W. Riener, *ibid.*, **67**, 723 (1945).

[21] R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," third ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 179.

[22] K. Alder and E. Windemuth, *Ber.*, **71B**, 2409 (1938).

b.p. 139–140° (11 mm.)). Oxidation of the liquid mixture gave an inhomogeneous ketone mixture, b.p. 78–87° (0.20 mm.), n^{25}D 1.5348, which was not studied further.

Oximes.—All of the ketones were converted to oximes by a standard procedure. A mixture of 0.40 mole of ketone, 34.0 g. (0.49 mole) of hydroxylamine hydrochloride, 52 ml. of pyridine and 300 ml. of absolute ethanol was refluxed for 12 hours. The ethanol was distilled on the steam-bath and 200 ml. of water was added to the cooled residue. The mixture was extracted twice with 150-ml. portions of methylene chloride. The organic extracts were dried and distilled.

Bicyclo[2:2:1]heptanone-2 Oxime (Ib).—Norcamphor (260.0 g., 2.36 moles) gave 265.6 g. of crude oxime, b.p. 81–86° (0.15 mm.) (lit.[23] b.p. 114–116° (12 mm.)) which solidified in the ice-box and remelted at room temperature, in agreement with reference 23. Crystallization from 400 ml. of hexane at −30°, followed by rapid filtering and pumping the precipitate dry, gave 246 g. of slightly sticky solid, m.p. 36.5–45°. This was pressed on a sintered glass funnel and drained under vacuum overnight, leaving 236 g. (79.7%) of a crisp white solid, m.p. 39–45°.

Anal. Calcd. for $C_7H_{11}NO$: N, 11.19. Found: N (Dumas), 11.22.

The infrared spectrum was consistent with the assigned structure, and showed no obvious impurities. By extensive recrystallization from hexane, accompanied by excessive loss of material, a small amount of crystalline solid was isolated, m.p. 50–51.5°.

Anal. Found: N, 11.23.

Performing the original oximation using sodium hydroxide instead of pyridine gave oxime identical in all respects with that described above.

Bicyclo[2:2:2]octanone-2 Oxime (XIb).—The oxime, approximate b.p. 116° (4.0 mm.), which crystallized immediately in the receiver, was obtained in 92.3% yield, m.p. 114–118° (lit.[14] m.p. 117–118°).

Bicyclo[3:2:1]octanone-2 Oxime (XVc) from Ketone Mixture XVa.—Ketone XVa (31.7 g., 0.255 mole) gave 34.2 g. of mixed oxime, b.p. 99–103° (2.5 mm.), as a semi-solid slush. Hexane, 25 ml., was added and the mixture was warmed to effect dissolution and allowed to crystallize in the ice-box. Filtration gave 13.6 g. of damp crystals, m.p. 75–77°. Recrystallization from 30 ml. of hexane gave 7.32 g. (19.5%) of white crystals, m.p. 93.5–94.5°.

Anal. Calcd. for $C_8H_{13}ON$: N, 10.06. Found: N (Dumas), 10.68.

Bicyclo[3:2:1]octanone-2 Oxime (XVc) from Ketone Mixture XVb.—The ketone (10.7 g., 0.0862 mole), gave 8.6 g. of oxime, b.p. 106–107° (2.3 mm.), as a white solid, m.p. 88–90°. Recrystallization from 32 ml. of hexane gave 5.54 g. (46.3%) of white crystals, m.p. 92–93.5°.

Anal. Calcd. for $C_8H_{13}ON$: N, 10.06. Found: N (Dumas), 10.81.

A mixed melting point with the preceding oxime preparation was 92.5–93.5° and the infrared spectra were identical and indicated homogeneity of the samples.

Nortricyclanone Oxime (IXb).—The ketone (95.0 g., 0.88 mole) led to 88.0 g. of the crude oxime, b.p. 78–81° (0.35 mm.), as a colorless viscous liquid. It partly crystallized from 25 ml. of hexane when stored at 4° overnight. Recrystallization of 86.1 g. of solid, m.p. 49–53°, from 160 ml. of hexane (some difficulty with oiling out) gave, after vacuum drying, 81.0 g. (74.8%) yield of white crystals, m.p. 59.0–60.5°.

Anal. Calcd. for C_7H_9ON: N, 11.37. Found: N (Dumas), 11.56.

4,7-Methano-3a,4,5,6,7,7a-hexahydroindene-5-one Oxime (IIIb).—The ketone (237.3 g., 1.60 moles) gave 221.5 g. of the crude oxime as a colorless viscous liquid, b.p. 95–98° (0.25 mm.) (lit.[20] b.p. 136–139° (4–5 mm.)). Crystallization from 150 ml. of hexane at 4° gave 168.4 g. (64.5%) of oxime, m.p. 95–96° (lit.[20] m.p. 105–106°).

4,7-Methanohexahydroindan-5-one Oxime (Vb).—The ketone (126.7 g., 0.844 mole) gave 133.7 g. of the crude oxime, b.p. 111–113° (0.35 mm.) (lit.[20] b.p. 130–135° (4 mm.)). Crystallization from 200 ml. of hexane gave 115.3 g. (82.7%), m.p. 81–82° (lit.[20] m.p. 87–88°).

1,4,5,8-Bis-endomethano-2-decalone Oxime (VIIb).—The ketone (96.9 g., 0.55 mole) gave rise to 94.0 g. of the crude oxime, b.p. 108° (1.5 mm.) −142° (0.75 mm.), as a viscous colorless liquid. It was diluted with 100 ml. of hexane and allowed to crystallize at 4° to give 66.8 g. of solid, m.p. 90–92°. A final crystallization of 66.8 g. from 180 ml. of hexane gave 52.0 g. (49.4%) of oxime, m.p. 105–107°.

Anal. Calcd. for $C_{12}H_{17}ON$: N, 7.32. Found: N (Dumas), 7.38.

3-Cyclohexenecarboxamide.—The addition of butadiene to acrylamide was performed at 140° during 15 hours. The product was washed thoroughly with water, dried, and sublimed at 160° (0.25 mm.) to give a 34.6% yield, m.p. 154–155°.

Anal. Calcd. for $C_7H_{11}ON$: N, 11.2. Found: N, 11.1, 11.2.

Bicyclo[2:2:1]hept-5-ene-2-carboxamide was prepared similarly at 180°. Working up as above gave a 38.7% yield, m.p. 160–171° (lit.[24] m.p. 181–183° when crystallized from water).

3-Piperidinepropionic Acid.—3-Pyridinecarboxaldehyde (Aldrich Chemical Co.), 100 g., was condensed with 102 g. of malonic acid using 200 ml. of pyridine and 4 ml. of piperidine under conditions similar to those of reference 25. The crude product, 116.3 g., was recrystallized from a mixture of 200 ml. of water and 550 ml. of dimethylformamide to give 108.6 g. (78.0% of 3-pyridineacrylic acid, m.p. 235–235.5° (lit. m.p. 233°,[26a] 231–234°.[26b]

This acid (50 g., 0.335 mole) was hydrogenated in 100 ml. of water over ruthenium dioxide. The catalyst was filtered through Celite and the filtrate was concentrated to a colorless sirup on the steam-bath under aspirator vacuum. Addition of 500 ml. of acetone and scratching caused it to crystallize over a 5-hour period. The solid was filtered, rinsed with acetone, and dried to provide 43.5 g. (82.6%) of white 3-piperidinepropionic acid, m.p. 178–179°. The infrared spectrum was consistent with the assigned structure and showed that no unsaturated groups were present. The preparation of high polymer from this material (see below) indicated that a negligible amount of starting material was present.

Anal. Calcd. for $C_8H_{15}O_2N$: C, 61.12; H, 9.62; O, 20.35. Found: C, 60.43; H, 9.71; O, 20.31.

3-Amino-4-methylcyclohexane Carboxylic Acid.—Nitration of *p*-toluic acid provided 3-nitro-4-methylbenzoic acid.[27] Hydrogenation of this acid in water over ruthenium-on-charcoal proceeded poorly in three runs. Thus 38.0 g. (0.210 mole) upon hydrogenation gave, after filtration, evaporation of the water under vacuum, and precipitation with acetone, 4.62 g. (14.0%) of white solid XXII, m.p. 250° dec. on a heated bar.

Anal. Calcd. for $C_8H_{15}O_2N$: N, 8.9. Found: N (Dumas), 9.18.

Lactams. *Via* **Beckmann Rearrangements.**—All of the oximes were rearranged by the method of Gates and Malchick.[2] To a stirred mixture of the oxime, 0.22 mole, in 300 ml. of 5 *N* sodium hydroxide solution, was added 41 g. (0.24 mole) of benzenesulfonyl chloride. The addition required 0.5–1 hour and the temperature was not allowed to exceed 50°. After an additional 0.5–1 hour, the mixture was extracted with 100-ml. portions of chloroform until no more lactam was extracted. The chloroform layers were dried over magnesium sulfate and distilled in a Claisen flask.

The olefinic nitrile was formed as a by-product of the lactam in most cases. They were not investigated, except for the one from bicycloheptanone. The odor of the nitrile from nortricyclanone induced dizziness in one observer, so these compounds should be handled in a hood.

Oximes IIIb and Vb with polyphosphoric acid gave only 10–15% yields of lactam.

2-Azabicyclo[3:2:1]octan-3-one (II).—Oxime Ib (55.1 g., 0.44 mole) gave 13.8 g. of nitrile, b.p. 150–185° (23

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TABLE IV

POLYMERIZATIONS

Lactam or aminoacid	Weight, g.	Catalyst	Temp., °C.	Time, hr.	Polymer, wt. g. (%)	M.p., °C.	η_{inh} (*m*-cresol)
XII	1.09	H_2O–H_3PO_4	223	25	1.04 (95.4)	212	0.19
XIX	1.50	H_2O–H_3PO_4	223	8.5	1.32 (88.0)	222	.35
3-Piperidinepropionic acid	4.00	H_2O–H_3PO_4	270	1.0[a]	3.40 (96.5)[b]	Glass	.51

[a] Water removed at 15 mm. pressure. [b] No solvent extraction was performed.

mm.), and 20.9 g. (38.0%) of lactam, b.p. 107–112° (0.75 mm.), n^{25}D 1.5142, as a colorless viscous liquid.

Anal. Calcd. for $C_7H_{11}ON$: N, 11.19. Found: N, 11.05.

A vapor phase chromatogram revealed two major peaks comprising 31.8 and 63.1% of the total, respectively. The infrared spectrum was consistent with the lactam formulation.

This material, 61.8 g., was distilled in a 70-cm. spinning band column at a reflux ratio of 15-1. The temperature gradually rose from 100–109° (0.45 mm.) and 1–3 g. fractions were taken arbitrarily. Vapor phase chromatograms of selected fractions were made on a 10-foot firebrick column using silicone grease at 181°. It was found that several impurities were present in the initial fractions, and that these gave way to a two-component mixture by fraction 8. From cut 8 the purity of the major component increased from 80.1 to 89.3% at fraction 15, then declined slowly to 78.7% at fraction 30. Various fractions from 8 to 30 were tested for polymerizability. A central fraction, 14, had n^{25}D 1.5153.

Anal. Found: N, 10.85.

The olefinic nitrile from oxime Ib was purified according to Gates and Malchick using Girard P reagent. The pure (56% recovery from crude material) nitrile distilled sharply at 92° (28 mm.), n^{25}D 1.4613, and appeared homogeneous.

Anal. Calcd. for C_7H_9N: N, 13.07. Found: N (Dumas), 12.92.

Sulfuric acid[3] was also employed for rearrangement. Oxime Ib (10.0 g., 0.080 mole) was slowly added with stirring and cooling in ice to 12.0 g. of 85% sulfuric acid. The resulting sirup was added to 5.0 g. of 85% sulfuric acid at 90–95° over 12 minutes with stirring and rinsed in with 2.0 g. of acid. After 5 more minutes at 90° the solution was cooled and added to 25.0 g. of ice. The solution was neutralized with 40 ml. of 29% ammonium hydroxide, keeping the temperature below 25°. The solution was extracted three times with 50-ml. portions of chloroform. The organic layers were dried and distilled to give 4.1 g. of inhomogeneous liquid, b.p. 116–119° (0.45 mm.). A vapor phase chromatogram showed: peak 1, 18.2%; peak 2, 10.0%; peak 3, 6.5%; peak 4, 29.4%; peak 5, 5.9%; peak 6, 15.3%; and peak 7, 14.7%. The material was not examined further. These results are in contradiction of those described in reference 3.

3-Aza-$\Delta^{8,9}$-tricyclo[5:3:0:1^{2,6}]undecan-4-one (IV).—Oxime IIIb (69.2 g., 0.424 mole) gave 10.1 g. of nitrile, b.p. 58–113° (0.25 mm.), and 40.4 g. of crude lactam, b.p. 133–140° (0.25 mm.). This was diluted with 50 ml. of hexane and allowed to crystallize in the ice-box. Filtration and draining on a sintered glass funnel to room temperature gave 29.4 g. of sticky white solid. Two crystallizations from 75-ml. portions of ether gave 21.2 g. (30.6%) of white crystals, m.p. 84.0–85.5° (lit.[2] m.p. 80–81°).

3-Azatricyclo[5:3:0:1^{2,6}]undecan-4-one (VI).—Oxime Vb (63.9 g., 0.387 mole), gave nitrile, 7.9 g., b.p. 67–93° (0.60 mm.), and lactam, 38.8 g., b.p. 133–143° (0.50 mm.), which crystallized on keeping. Two recrystallizations from 75-ml. portions of ether gave 27.8 g. (43.5%) of lactam, m.p. 100–100.5°, mixed melting point with lactam IV, 59–72°.

Anal. Calcd. for $C_{10}H_{15}ON$: N, 8.48. Found: N, 8.25.

3-Azatetracyclo[5:4:0:1^{2,6}:1^{8,11}]tridecan-4-one (VIII).—Oxime VIIb (40.2 g., 0.21 mole) gave on distillation, a forerun, 7.4 g., b.p. 83–140° (0.25 mm.), consisting mainly of nitrile; and a main fraction, 19.8 g., b.p. 169–173° (0.25 mm.), which solidified in the receiver. The latter was triturated thoroughly with 25 ml. of warm hexane, cooled, and filtered. The lactam, 16.9 g. (42.0%), melted at 168–169.5°.

Anal. Calcd. for $C_{12}H_{17}ON$: N, 7.32. Found: N, 7.23.

3-Azatricyclo[3:2:1:0^{4,6}]octan-2-one (X).—Oxime IXb (74.7 g., 0.607 mole) gave 59.1 g. of crude lactam, b.p. 65° (3.6 mm.)-127° (1.0 mm.), which crystallized in the receiver. Trituration with 150 ml. of ether and filtration gave 31.7 g. of white solid. Sublimation at 205° (0.35 mm.) gave, after a little liquid had condensed and had been discarded, 28.3 g. (37.9%) of dense white solid, m.p. 173.0–174.5°.

Anal. Calcd. for C_7H_9ON: N, 11.37. Found: N, 11.32.

2-Azabicyclo[3:2:2]nonan-3-one (XII).—Oxime XIb (25.0 g., 0.180 mole), gave 20.9 g. of crude lactam, b.p. *ca.* 130° (0.45 mm.), solidifying to a waxy solid. This was placed in a small spinning band column and the nitrile was distilled at 42° (0.25 mm.) and discarded. The residue was redistilled to give 14.5 g. of white crystals. Crystallization from hexane at −80° gave, in two crops, 8.55 g. of lactam, which in final crystallization from 30 ml. of ether at −80° gave 6.35 g. (25.4%) of white crystals, m.p. 159–159.5°.

Anal. Calcd. for $C_8H_{13}NO$: N, 10.06. Found: N, 9.89.

This lactam was 98.2% pure by vapor-phase chromatography. The infrared spectra was identical with that of the sample prepared previously from 4-aminocyclohexylacetic acid.[1]

2-Azabicyclo[4:2:1]nonan-3-one (XIX).—Oxime XVc (11.45 g., 0.0821 mole), gave lactam, b.p. 110° (0.25 mm.), 7.9 g., as a semi-solid mass. This was redistilled in a small spinning band column. After 0.55 g. of forerun, the lactam, 4.25 g., b.p. 119° (0.70 mm.), was taken. It solidified to white crystals in the receiver, which were triturated with 10 ml. of hexane and filtered to give 3.75 g. (32.8%) of white crystals, m.p. 85–87°.

Anal. Calcd. for $C_8H_{13}ON$: N, 10.06. Found: N, 9.79.

Via **Amino Acids. 4-Methyl-6-azabicyclo[3:2:1]octan-7-one (XXI).**—Amino acid XX (19.6 g., 0.125 mole) was heated in a distilling flask at 8 mm. with a pale blue flame. Water was evolved and the lactam distilled smoothly. It was taken up in methylene chloride, dried, and redistilled, b.p. 106° (0.40 mm.), to give 12 g. of yellow oil which crystallized on keeping. Recrystallization from 25 ml. of hexane gave 9.10 g. (52.3%) of white crystals, m.p. 65–66.6°.

Anal. Calcd. for $C_8H_{13}ON$: N, 10.1. Found: N, 9.8, 9.9.

This may be a mixture of isomers, since the infrared C=O band split in three using high resolution.

Via **Ritter Reactions.**—Cyclopentenylacetonitrile, the by-product from the Beckmann rearrangement of norcamphor, was recovered (70.7%) from an attempted cyclization according to reference 28. Concentrated sulfuric acid gave some crystalline material from 3-cyclohexenecarbonitrile, but none from bicycloheptenecarbonitrile; however, the matter was not pursued.

Via **Olefinic Amides.**—Heating 3-cyclohexenecarboxamide and bicycloheptenecarboxamide with a little sodium hydride with or without added N-acetylcaprolactam at 150–200° for 7 hours gave only recovered starting material.

Polymerizations.—Polymerizability was studied using two drops of a 20% dispersion of sodium hydride plus one drop of acetic anhydride for 4 g. of lactam at temperatures from the lactam melting point to 270°; and using one drop of water plus one drop of 85% phosphoric acid for 4 g. of lactam from 180–230°. A nitrogen atmosphere was used in each case. Under the former conditions, caprolactam polymerized in a matter of minutes at 156° to poly-6-caproamide in 96% yield, m.p. 230°, η_{inh} 1.26 (*m*-cresol). Under the latter conditions, an 81% yield of poly-6-caproamide was formed in 6 hours at 200°, m.p. 230°, η_{inh} 0.46 (*m*-cresol).[6]

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(28) J. J. Ritter and P. P. Minieri, THIS JOURNAL, **70**, 4045, 4048 (1948).

Polymerization was observed as an increase in viscosity of the molten lactam or as formation of a glass or a solid mass. The tubes were cooled, broken, open, extracted with water and acetone and dried.

The following lactams and amides were unchanged under the polymerization conditions except for darkening. No viscosity increase or formation of solid or glass were observed, and the products always dissolved readily in acetone–water mixtures; II, IV, VI, VIII, X and XXI.

The inherent viscosity is defined as ($\ln \eta_{\text{rel}})/c$, where c is 0.5 g. of polymer per 100 ml. of solution, or 2 in η_{rel}. The polymer melting temperature was determined approximately by pressing a small portion of polymer firmly with a spatula and moving it along a calibrated heated bar. The temperature at which the turbid, opaque trail on the bar gave way to a clear melt was taken as the melting point.

The polymers of Table IV were all soluble in sulfuric acid, *m*-cresol, 90 and 99% formic acids, chloroform–formic acid (60:40 by vol.) and trifluoroacetic acid, except that the polymer from XXVI gave two liquid phases in the last solvent.

Spectra.—The infrared spectra of all compounds encountered in this investigation were measured routinely and supported the proposed structures. In particular, all of the nortricyclene derivatives absorbed at 12.3–12.4 μ, as first noted by Roberts, *et al.*[19]

WILMINGTON, DEL.

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

Infrared Carbonyl and Carbon–Hydrogen Frequencies in Bridged Bicyclic Ketones

BY R. ZBINDEN AND H. K. HALL, JR.

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Infrared measurements of the C=O and C—H stretching frequencies of monocyclic and bridged bicyclic ketones have been made. The frequencies have been correlated with ring size and geometrical structure of the molecules.

In this paper we report infrared absorption measurements on the C=O and CH_2 stretching vibrational bands of monocyclic and bridged bicyclic ketones. The frequencies are correlated with ring size and geometrical structure of the molecules. The experimental results are summarized in Table I.

C=O Stretching Frequencies.—The discussion of the C=O stretching frequencies is straightforward in view of the results on other cyclic carbonyl compounds described in a previous paper,[1] wherein references to earlier work are given (see also ref. 2). The carbonyl frequency is known to increase with decreasing ring size by going from an open chain or 7-membered ring to a six-, five- and four-membered ring. The frequencies listed in Table II show that the same is true for bi- and tricyclic ketones, where the C=O frequency is determined by the size of the smallest ring (*cf.* ref. 1).

The frequency shifts are due to bond angle deformations. Halford[3] has given a formula for the frequency ν as a function of substituent bond angle φ

$$\nu(\text{in cm.}^{-1}) = 1278 + 68k - 2.2\ \phi \text{ in degrees}$$

where k is the carbonyl stretching force constant for an aliphatic ketone. He showed that $k = 10.2 \pm 0.3$ practical units ($= 10^{-5}$ dynes/cm.) and is almost independent of the bond angle φ. This means that the linear relationship can be used to calculate the bond angle φ from the observed frequencies. The results of such a calculation are listed in Table II in parenthesis behind the frequency values. The absolute error in ϕ is ±9° due to the uncertainty in k. However, the difference between any two angles listed in Table II should be much more precise.

CH_2 Stretching Vibrations.—Similarly, the CH_2 stretching frequencies can be correlated with ring size, more specifically with the bond angle of the CH_2 group substituents. This particularly has been noticed for cyclopropane rings[1,4,5] where this bond angle is reduced from 109 to 60°. Similar band shifts have also been observed for unsaturated CH stretching vibrations due to bond angle deformations.[6–8]

First we want to point out that the difference Δ (Table I) between the asymmetric and symmetric CH_2 stretching frequency is approximately constant and has a value between about 60 and 90 cm.$^{-1}$. This was also true for a number of compounds previously analyzed.[1] In some cases this rule of constant difference was actually used as a guide for band assignments. A qualitative explanation can be given as follows: Consider the two CH bonds in a CH_2 group as two coupled dipoles of the same frequency. Such a system has two normal vibrations, a symmetric and an antisymmetric one. The frequencies will split due to vibrational interaction. Reduction in substituent bond angle increases the force constant of both dipoles but does not change their interaction appreciably which means that the two components shift by about the same amount toward higher frequencies. For this reason the symmetric or the antisymmetric vibrational frequency could be used as a measure for bond angle deformations. In this work we have chosen to use their average (Table I) to get slightly better accuracy. It is the shift of this $\nu_{\text{av.}}$ which will be discussed in the following paragraphs.

We assume a linear relationship between the substituent bond angle and the average CH_2 frequency in analogy to the carbonyl band shifts. The

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