aqueous solution prepared from 10 g. of potassium bicarbonate. The resulting orange-brown suspension was heated on a steam bath for 1 hr. and cooled, and the solid which separated was collected. This, after being washed thoroughly with water and then air-dried, was recrystallized from benzene to give 3.8 g. (56%) of yellow crystals, m.p. 180–190° dec. Treatment with charcoal in acetonitrile followed by an additional recrystallization from benzene yielded white crystals, m.p. 180–190° dec. The ultraviolet absorption spectrum of II in ethanol showed a maxima at 254 mμ (log ε 4.74) with a shoulder at 258 mμ (log ε 4.72).

Anal. Calcd. for $C_{14}H_{12}N_2$: C, 80.74; H, 5.81; N, 13.45. Found: C, 80.67; H, 5.86; N, 13.23.

3,4-Dicarbethoxy-6-methyl-2-phenyl-5-azacycl[3.2.2]azine (III).—To a solution of 9.0 g. of 7-methyl-2-phenyl-6-azapyrrocoline (II) and 9.4 g. of dimethyl acetylenedicarboxylate in 540 ml. of toluene there was added 8.0 g. of a 5% palladium-on-charcoal catalyst, and the mixture was heated under reflux in a nitrogen atmosphere for 21 hr. After removal of the catalyst and solvent, the brown, gummy residue was taken up in benzene and passed over neutral alumina (800 g., grade III, Woelm). Following the initial eluate which contained 0.25 g. of II, the main fraction gave 4.15 g. (28%) of bright yellow crystals, m.p. 152–154°. A further recrystallization from ethyl acetate yielded yellow needles, m.p. 155–156°. The absorption spectrum of III in ethanol showed maxima at 242 (4.53), 266 (4.30), 336 (4.29), and 448 mμ (log ε 3.91).

Anal. Calcd. for $C_{20}H_{16}N_2O_4$: C, 68.96; H, 4.63; N, 8.04. Found: C, 68.77; H, 4.75; N, 7.87.

3,4-Dicarboxy-6-methyl-2-phenyl-5-azacycl[3.2.2]azine (IV).—A mixture of 150 mg. of III and 30 ml. of methanol saturated with potassium hydroxide was heated at 50° with stirring until complete solution resulted (30 min.), whereupon precipitation of the dipotassium salt of IV occurred. The mixture was heated for an additional 30 min. before collecting the precipitate by filtration. The solid precipitate was redissolved in a minimum amount of water, and the solution was acidified with concentrated hydrochloric acid. There separated 130 mg. (95%) of yellow crystals, m.p. 230–235°.

Anal. Calcd. for $C_{18}H_{12}N_2O_4$: C, 67.50; H, 3.78; N, 8.75. Found: C, 67.20; H, 3.98; N, 8.58.

When the diacid IV was recrystallized from pyridine, the monopyridinium salt of IV separated as long, orange needles, m.p. 170° dec.

Anal. Calcd. for $C_{23}H_{17}N_3O_4$: C, 69.16; H, 4.29; N, 10.52. Found: C, 69.07; H, 4.42; N, 10.55.

6-Methyl-2-phenyl-5-azacycl[3.2.2]azine (V).—A mixture of 900 mg. of the crude diacid IV and 1.0 g. of copper powder in 250 ml. of aniline was boiled under reflux until evolution of carbon dioxide ceased. After removal of the catalyst and concentration under reduced pressure, the gummy residue was taken up in benzene and chromatographed over Florisil (300 g.). From the third fraction of eluate there was obtained 510 mg. (78%) of an orange-yellow solid, m.p. 135–140°. Recrystallization from an ether-pentane mixture (1:1) produced large, yellow-orange crystals, m.p. 145–147°. The n.m.r. spectrum in methylene chloride showed a proton signal for the methyl group at 7.18 τ. In concentrated sulfuric acid this signal was shifted to 6.77 τ with two smaller additional signals at 6.70 and 7.03 τ. The latter two signals are presumably due to protonation on carbon at the 1- and 4-positions.[8]

Anal. Calcd. for $C_{16}H_{12}N_2$: C, 82.73; H, 5.21; N, 12.06. Found: C, 82.86; H, 5.28; N, 11.90.

Synthesis and Polymerization of 3-Azabicyclo[4.3.1]decan-4-one and 7,7-Dimethyl-2-azabicyclo[4.1.1]octan-3-one

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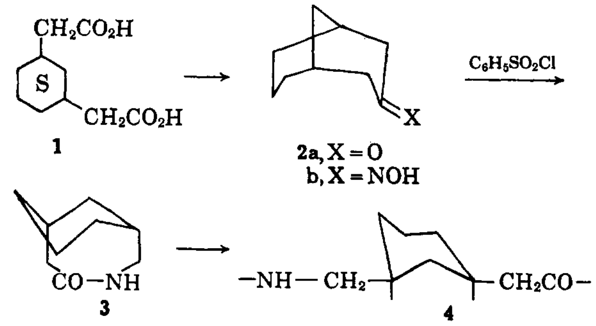
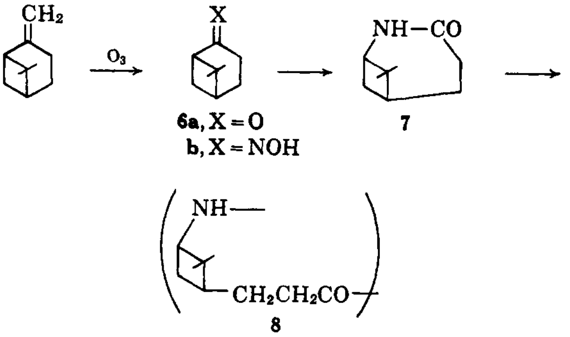
Cyclohexane-1,3-diacetic acid readily cyclized to bicyclo[3.3.1]nonan-3-one (**2a**) when heated with barium oxide. Hydroxylamine converted the ketone to the oxime **2b**, which underwent the Beckmann rearrangement to give the desired lactam, 3-azabicyclo-[4.3.1]decan-4-one (**3**). Cyclohexane-1,4-diacetic acid, under conditions which readily cyclized the 1,3-isomer, gave no bicyclo[3.2.2]nonan-3-one (**5**). The ketone **2a** can exist in a stable two-chair conformation, while **5** would possess a strained boat form of the cyclohexane ring. This difference in conformation may account for the difference in ease of formation of the two ketones.



Nopinone (**6a**) recently has been made available[1] by ozonolysis of β-pinene. This preparation was repeated and the ketone was converted to the oxime **6b** and thence by Beckmann rearrangement to a crystalline lactam. The oxime is assigned the configuration with the hydroxyl group *anti* to the cyclobutane ring, since this configuration is sterically less strained than the *syn* form. Because of the *trans* nature of the rearrangement, the lactam is assigned the structure 7,7-dimethyi-2-azabicyclo[4.1.1]octan-3-one (**7**). This type of assignment, applied previously to other atom-bridged oximes and lactams,[2] was shown subsequently to be correct by degradation studies.[3]



Polymerizations.—The lactams were converted to polyamides by heating at 200–223° with 5% of 85% phosphoric acid as catalyst.[2,4] Lactam **3** polymerized much more readily than lactam **7**. Hydrogen crowding within the bridged rings is considered to be the destabilizing factor in these molecules which causes them to polymerize. Like many other polyamides possessing alicyclic rings in the polymer chain,[2,4] these polymers displayed quite high melting points; **4** melted at 297° and **8** at 358°.

Experimental

Cyclohexane-1,3- and 1,4-diacetic Acids.—Pure *m*-phenylenediacetic acid was not available but an approximately 1:1 mixture

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[1] J. Meinwald and P. G. Gassman, *J. Am. Chem. Soc.*, **82**, 5445 (1960).

[2] H. K. Hall, Jr., *ibid.*, **82**, 1209 (1960).

[3] R. C. Elderfield and E. T. Losin, *J. Org. Chem.*, **26**, 1703 (1961).

[4] H. K. Hall, Jr., *J. Am. Chem. Soc.*, **80**, 6412 (1958).

of *m*- and *p*-isomers (du Pont Electrochemicals Department RH-870) was on hand. A mixture of 315 g. of this acid, 520 ml. of ethanol, and 2.5 l. of benzene was brought to boiling and stirred for 1 hr. The mixture was chilled and filtered. There was recovered 117 g. of almost pure *p*-isomer, m.p. 255°, m.m.p. 255° on a heated bar (lit.[5] m.p. 244°). The filtrate was concentrated to a small volume. Ethanol, 1.2 l., was added and the mixture was saturated with hydrogen chloride gas. After 20 hr. it was distilled to give 217 g. of diethyl phenylenediacetates, b.p. 127–130° (1.1 mm.). Hydrogenation was performed over 3 g. of ruthenium dioxide in 250 ml. of ethanol at 135° and 1565 p.s.i. Hydrogen, 1.4 moles (54%), was absorbed. Rehydrogenation resulted in no further uptake. The product, 174.5 g., boiled at 115–133° (0.15 mm.). The infrared spectrum showed the presence of ester groups and absence of aromatic or unsaturated links. The diester, 70.0 g., was boiled under reflux for 5 hr. with 70 g. of sodium hydroxide, 200 ml. of ethanol, and 300 ml. of water. The ethanol was distilled, and the residue was cooled and acidified with 12 *N* hydrochloric acid. After 3 days, the precipitate was filtered, rinsed with water, and air dried to give 51.0 g. of mixed cyclohexane-1,3- and 1,4-diacetic acids, m.p. 130–132°.

Anal. Calcd. for $C_{10}H_{16}O_4$: C, 60.0; H, 8.1. Found: C, 59.7; H, 8.1.

Bicyclo[3.3.1]nonan-3-one (2a).—The mixture of cyclohexanediacetic acids, 26.0 g. (0.13 mole), was mixed with 50 ml. of acetic anhydride, and acetic acid was distilled over a 1-hr. period. The remainder was distilled through a Claisen head at 150 mm. using a pale blue flame. The distillate was taken up in 100 ml. of ether and washed with 100 ml. of water and with 150 ml. of 15% sodium carbonate solution. The aqueous layers were back extracted with 50 ml. of hexane. The organic layers were dried and the solvents were evaporated. Short-path distillation of the residue at 15 mm., followed by crystallization of the residue at −80° from hexane, gave 4.6 g. of an off-white solid. Sublimation at 140° (18 mm.) gave 4.06 g. (22.6%) of pure ketone, m.p. 180–182°. The use of barium oxide in place of acetic anhydride in the distillation gave a lower yield of the same ketone.

Anal. Calcd. for $C_9H_{14}O$: O, 11.6. Found: O, 11.7.

The carbonyl group absorption in the infrared spectrum[6] of this ketone was split into two bands at 1706 and 1717 cm.$^{-1}$. The 2,4-dinitrophenylhydrazone[7] melted at 208–209° after one recrystallization from ethanol–ethyl acetate.

Similarly, esterification of pure *p*-phenylenediacetic acid gave diethyl ester, m.p. 59–59.5° (lit.[5] m.p. 59–59.5°); hydrogenation gave the diethyl ester of cyclohexane-1,4-diacetic acid; and hydrolysis provided cyclohexane-1,4-diacetic acid, m.p. 164–165°, which was analyzed.

Anal. Calcd. for $C_{10}H_{16}O_4$: C, 60. 0; H, 8.1. Found: C, 59.8; H, 8.2.

Distillation of the 1,4-diacid from barium oxide gave no ketonic product, proving that the ketone described above was derived from cyclohexane-1,3-diacetic acid.

Bicyclo[3.3.1]nonan-3-one Oxime (2b).—The crude oxime, b.p. 113–115° (1.0 mm.), 12.25 g., was obtained as described[2] from 12.79 g. (0.0925 mole) of ketone as a white solid in the receiver, m.p. 108–114°. Recrystallization from 30 ml. of hexane gave 10.10 g. (71.3%) of oxime, m.p. 108–109°.

Anal. Calcd. for $C_9H_{15}ON$: N, 9.14. Found: N (Dumas), 9.36.

3-Azabicyclo[4.3.1]decan-4-one (3).—The oxime **2b**, 9.92 g. (0.065 mole), led by Beckmann rearrangement[8] to a lactam which sublimed at 100–160° (0.45 mm.), 6.2 g. This was taken up in 25 ml. of hexane and crystallized at −80° to give 3.30 g. of white solid. Crop 2, 1.26 g., and crop 3, 0.98 g., were obtained by evaporation of the solvent and crystallization again at −80°. The combined yield was 55.9%.

Anal. Calcd. for $C_9H_{15}ON$: N, 9.14. Found: N, 8.84, (crop 1), 8.77 (crop 2), 8.73 (crop 3).

These fractions did not melt sharply but rather became semisolid at 80–120°. They were evidently polymerizing during the determination.

Nopinone Oxime (6b).—"Sulfate" β-pinene, from Hercules Powder Co., was established as 91% pure by vapor phase chromatography. It was ozonized as described by Meinwald and Gassman[1] to give nopinone, b.p. 92° (16 mm.), 99+% pure by v.p.c. The oxime was prepared as described.[2] Distillation of the oxime prepared from 38.2 g. of nopinone gave 40.1 g., b.p. 107° (1.5 mm.). It crystallized slowly and completely. Recrystallization from 20 ml. of heptane gave 33.2 g. oxime, m.p. 61.5–65.0°.

Anal. Calcd. for $C_9H_{15}ON$: C, 70.55; H, 9.87; N, 9.14. Found: C, 70.50, 70.46; H, 9.99, 10.06; N, 8.86, 8.97.

7,7-Dimethyl-2-azabicyclo[4.1.1]octan-3-one (7).—The Beckmann rearrangement of 23.1 g. of oxime was carried out using sodium hydroxide and benzenesulfonyl chloride.[8] The chloroform extract was concentrated and diluted with 800 ml. of ether. Flocculent material was filtered. The filtrate was concentrated and distilled at 0.3 mm. up to 130°. The distillate solidified in the receiver and considerable undistillable residue remained. After three sublimations and crystallization from 15 ml. of heptane, the lactam weighed 9.85 g. (42.6%) and melted at 111.0–113.0°.

Anal. Calcd. for $C_9H_{15}ON$: C, 70.6; H, 9.9; N, 9.14. Found: C, 70.5, 70.3; H, 9.9, 9.9; N, 8.91, 8.91.

The infrared spectrum was consistent with that of a lactam, although no 6.50-μ band was observed.

Polymerizations.—Lactam **3**, 1.50 g., was polymerized by heating with 1 drop of water and 1 drop of 85% phosphoric acid[2,4] in a sealed glass tube under nitrogen for 8.5 hr. at 223°. The polyamide 4 of *cis*-3-aminomethylcyclohexylacetic acid weighed 1.32 g. (88.0%) after washing with water and acetone. It melted at 297° and had an inherent viscosity in *m*-cresol of 0.21.

Lactam **7** was polymerized similarly by 5% of 85% phosphoric acid at 200° for 17 hr., and a 75% yield of product was obtained after methanol extraction. The polyamide **8** of *cis*-3-amino-2,2-dimethylcyclobutanepropionic acid melted at 358° and possessed an inherent viscosity of 0.62 in *m*-cresol. The use of less phosphoric acid for longer times led to lower molecular weight polymer, while the use of sodium hydride–acetic anhydride gave only dark oils.

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[8] M. Gates and S. P. Malchick, *J. Am. Chem. Soc.*, **79**, 5546 (1957).

Products from the Acetolysis of (−)-(S)-Bicyclo[2.2.2.]octyl-2 *p*-Bromobenzenesulfonate. A Reinvestigation[1]

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In a previous publication[2] it was reported that acetolysis of (−)-bicyclo[2.2.2]octyl-2 *p*-bromobenzenesulfonate resulted in a mixture of (+)-acetates which upon reduction with lithium aluminum hydride yielded a mixture of alcohols consisting of 65 ± 3% bicyclo-[2.2.2]octanol-2 and 35 ± 3% of axial bicyclo[3.2.1]-octanol-2. The mixture was separated using preparative vapor phase chromatography, but only 4–6-mg. quantities of each component were isolated in a pure state, since the peaks overlapped considerably because

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[1] This work was supported by research grant Cy-4065, National Institutes of Health, Public Health Service.

[2] H. M. Walborsky, M. E. Baum, and A. A. Youssef, *J. Am. Chem. Soc.*, **83**, 988 (1961).