rated solution was heated to boiling on a steam bath and clarified with charcoal. The volume of solution was reduced by air blowing while the sides of the flask were scratched vigorously. When a substantial amount of solid had separated, the contents were filtered under suction and the solid was dried under reduced pressure. Additional solid was obtained from the filtrate by repeating the above procedure. The photodimer was crystallized twice to yield a white solid, m.p. 209–210°, λ_{max}^{EtOH} only end absorption, $\nu_{max}^{CH_2Cl_2}$ 1785 and 1650 cm.$^{-1}$.

Anal. Calcd. for $(C_{11}H_9NO_2)_2$: C, 70.58; H, 4.84; mol. wt., 374.4. Found: C, 70.77; H, 5.18; mol. wt. (Rast), 386.

The rate of photodimerization was significantly increased by irradiation of the pseudoxazolone with visible or ultraviolet light. Two grams of I was placed on a sheet of aluminum foil and spread out to allow maximum surface exposure. The pseudoxazolone was irradiated with ultraviolet light (quartz lamp) for 2 days with frequent mixing of the solid in order to provide a fresh surface. Sublimation of the irradiated product gave 0.3 g. (15%) of dimer. The process was repeated to give additional product.

Infrared spectra were obtained on a Perkin–Elmer Model 21 double beam spectrophotometer equipped with sodium chloride optics. Ultraviolet spectra were measured with a Beckman DK-2 recording spectrophotometer. Proton magnetic resonance spectra were determined on a Varian Associates A-60 spectrometer.

Microanalyses were conducted by Micro-Tech Laboratories, Skokie, Illinois.

Polymerization of Two Atom-bridged Bicyclic Amines

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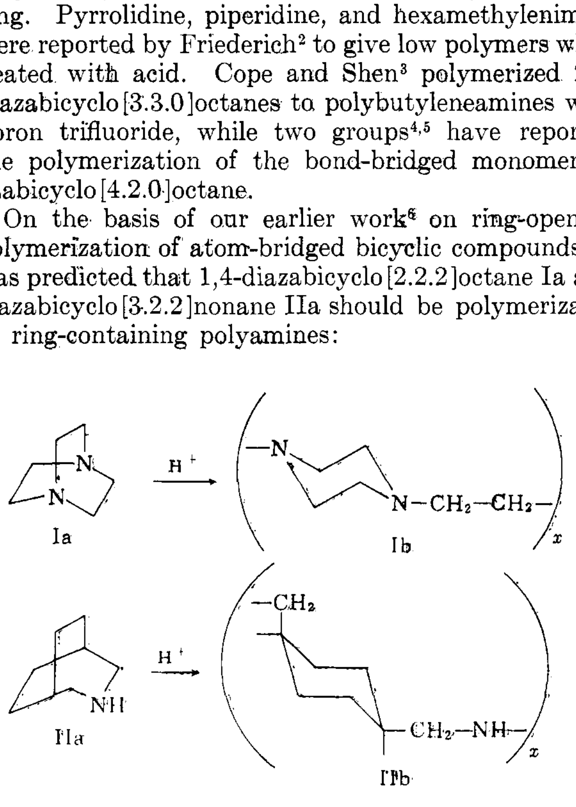
Relatively few ring-opening polymerizations of cyclic amines have been described. Ethylenimine polymerizes very readily[1] as would be expected for a highly strained ring. Pyrrolidine, piperidine, and hexamethylenimine were reported by Friederich[2] to give low polymers when heated with acid. Cope and Shen[3] polymerized 2,6-diazabicyclo[3.3.0]octanes to polybutyleneamines with boron trifluoride, while two groups[4,5] have reported the polymerization of the bond-bridged monomer 1-azabicyclo[4.2.0]octane.

On the basis of our earlier work[6] on ring-opening polymerization of atom-bridged bicyclic compounds, it was predicted that 1,4-diazabicyclo[2.2.2]octane Ia and 3-azabicyclo[3.2.2]nonane IIa should be polymerizable to ring-containing polyamines:

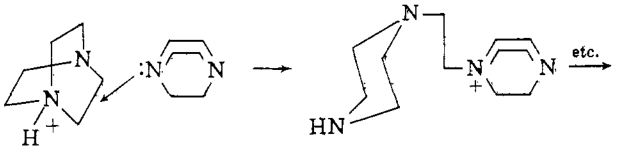


This proved to be the case.

Heating 1,4-diazabicyclo[2.2.2]octane for 10.7 hours at 200° with 0.073 mole % of benzenesulfonic acid converted the monomer to poly-1,4-ethylenepiperazine in 96% yield. The polymer Ib was a white, highly crystalline solid melting above 350° with decomposition.

3-Azabicyclo[3.2.2]nonane IIa polymerized less readily. Heating the monomer with 0.46 mole % of benzenesulfonic acid for 71 hours at 222° gave a 32% yield of polymer IIb, m.p. 115–130°.

The mechanism of the acid-catalyzed polymerization of amines probably involves nucleophilic attack by one amine molecule on the protonated or alkylated form of another:



Henecka and co-workers[7] have described analogous ring-openings of bicyclic ammonium ions by nucleophiles.

The strains which cause these bicyclic amines to polymerize are caused by repulsions between nonbonded hydrogens. The parent hydrocarbon bicyclo[2.2.2]-octane exists in a two-boat form.[8] The repulsions of the hydrogens in the bridges destabilize the molecule. Since 1,4-diazabicyclooctane exists in the same conformation and is similarly destabilized, its tendency to polymerize is expected. 3-Azabicyclo[3.2.2]nonane undergoes polymerization less readily because it thereby relieves only one strained boat cyclohexane ring by converting it to a chair form.

Experimental

Monomers.—1,4-Diazabicyclo[2.2.2]octane was obtained from the Houdry Process Corporation and 3-azabicyclo[3.2.2]nonane from the Tennessee Eastman Co. Both were sublimed at 100° (15 mm.) before use.

For convenience in manipulation the benzenesulfonic acid was supplied as the salt of the amine.

Catalysts.—The di(hydrobenzenesulfonate) of Ia was prepared by mixing 35.3 g. (0.20 mole) of redistilled benzenesulfonic acid and 11.22 g. (0.10 mole) of diazabicyclooctane in 350 ml. of ethyl acetate. The white precipitate was filtered and recrystallized from 800 ml. of ethanol to give 31.6 g. (73.7%) of white crystals of the di(hydrobenzenesulfonate), m.p. 297° on a heated bar.

Anal. Calcd. for $C_{18}H_{24}O_6N_2S_2$: C, 50.5; H, 5.64; N, 6.54. Found: C, 48.90, 49.02; H, 5.55, 5.59; N, 6.53, 6.64.

The hydrobenzenesulfonate of II was prepared by mixing 12.62 g. (0.1 mole) of amine and 15.82 g. (0.10 mole) of redistilled

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(1) W. G. Barb, *J. Chem. Soc.*, 2564, 2577 (1955), and references cited therein.

(2) H. Friederich, German Patent 1,037,126 (1958).

(3) A. C. Cope and T. Y. Shen, U. S. Patent 2,932,650 (1960).

(4) E. R. Lavagnino, R. R. Chauvette, W. N. Cannon, and E. C. Kornfeld, *J. Am. Chem. Soc.*, **82**, 2609 (1960).

(5) M. S. Toy and C. C. Price, *ibid.*, 2613.

(6) H. K. Hall, Jr., *ibid.*, **80**, 6412 (1958).

(7) H. Henecka, V. Hoerlein, and K. H. Risse, *Angew. Chem.*, **72**, 960 (1960).

(8) P. R. Schleyer, R. D. Nicholas, and F. Fong, *J. Am. Chem. Soc.*, **83**, 2705 (1961), footnote 44. Since the lone pair electrons of nitrogen appear to be bulkier than hydrogen [M. Aroney and R. J. W. LeFevre, *Proc. Chem. Soc.*, **82** (1958)], 1,4-diazabicyclooctane should also exist in the opposed conformation. The proposal that quinuclidine exists in a twisted conformation [Z. Foldi, T. Foldi, and A. Foldi, *Chem. Ind.* (London), 465 (1957)] may be modified slightly to state that twisting can be achieved by chelation or other bond formation.

benzenesulfonic acid in 125 ml. of ethyl acetate. The precipitate was crystallized from ethyl acetate–ethanol (8:1) to give 19.9 g. (70.3%) of very slightly pink crystals, m.p. 123.5–124.5°.

Anal. Calcd. for $C_{14}H_{21}O_3NS$: C, 59.33; H, 7.47; N, 4.94. Found: C, 59.19, 59.07; H, 7.32, 7.30; N, 4.70, 4.69.

Polymerizations.—The amine and catalyst were weighed into a 23 × 196 mm. test tube under nitrogen. This was chilled to −80°, alternately evacuated and flushed with nitrogen, and was finally evacuated and sealed. The ampules were suspended in the vapor of boiling *m*-cresol or methyl salicylate to maintain them at 200° or 222°, respectively. They were shaken after a few minutes to ensure dissolution of the catalyst.

Under these conditions, a mixture of 10.0 g. of 1,4-diazabicyclooctane and 27.8 mg. of its di(hydrobenzenesulfonate) polymerized rather quickly at 200°. A solid white plug was noted after 1 hr., but heating was continued for an additional 9.7 hr. The tough white plug was broken up with a knife and hammer and extracted with ether to give 9.60 g. (96%) of white polymer, η_{inh} (*m*-cresol) 1.90. On a heated bar it blackened at 250° but did not melt below 390°.

Anal. Calcd. for $(C_6H_{12}N_2)_x$: C, 64.24; H, 10.79; N, 25.0. Found: C, 63.75, 63.76, 63.58, 63.48; H, 10.40, 10.47, 10.51, 10.41; N, 24.0, 24.3, 24.7.

A mixture of 10.0 g. of 3-azabicyclo[3.2.2]nonane and 105.1 mg. of its di(hydrobenzenesulfonate) became sirupy when heated for 71 hr. at 222°. Cooling, extraction of the product with ether, and drying gave 3.20 g. (32%) of white polymer, polymer melt temperature 115–130°.

Anal. Calcd. for $(C_8H_{16}N)_x$: C, 77.99; H, 10.63. Found: C, 75.95, 75.72; H, 11.79, 11.77.

The polymer appeared to be hygroscopic.

Polymer Properties.—Poly-1,4-ethylenepiperazine was obtained as an extremely crystalline white solid, insoluble in nonpolar organic solvents. A typical sample had an inherent viscosity of 1.06 in *m*-cresol and 2.11 in 99% formic acid. The end groups were determined by reaction with 2,4-dinitrofluorobenzene. A polymer of inherent viscosity 1.77 had a number average molecular weight of 8800, assuming reaction at only one end of the chain. The infrared spectrum was very similar to that of the model compound, N,N'-dimethylpiperazine. It showed small amounts of NH and NH^+ but no vinyl groups, so that no ring cleavage had occurred. Refluxing the polymer with aqueous alkali did not decrease its inherent viscosity, so that cross-links by quaternary ammonium linkage were not present.

The polyamine from 3-azabicyclo[3.2.2]nonane had inherent viscosities of 0.30 in *m*-cresol, 0.37 in tetrafluoropropanol, and 0.46 in 99% formic acid.

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2,2'-Diindoxyls

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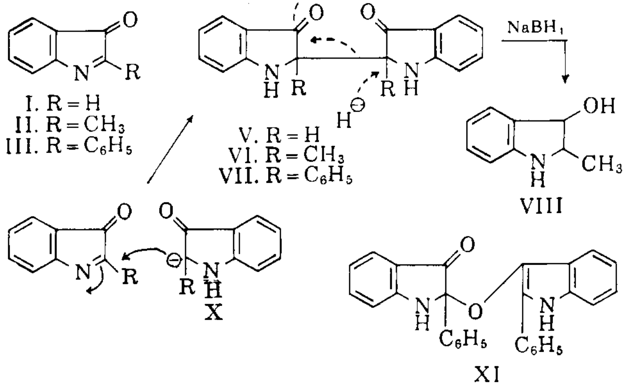
Indoxyl has long been known to be converted to indigo by air in the presence of sodium hydroxide,[2] but the presumed intermediate indoleninone (I) has never been isolated. Recently Neunhoeffer and Lehmann[3] reported the isolation of what they believed to be an indoleninone, namely 2-methylindoleninone (II), as a stable compound. The compound had a molecular weight of 280 in boiling dioxane (calcd. 147) and no spectroscopic data were reported to substantiate the assigned structure. The indoleninone was obtained from ethyl α-(2-carbethoxyanilino)propionate upon Dieckmann condensation, decarbethoxylation and air oxidation of the intermediate 2-methylindoxyl without isolation of intermediates.[2] Our experience with 2-substituted indoxyls[4] suggested that compounds of type II are very unstable and can not be isolated. Furthermore, in 1912, Kalb and Bayer[5] reported 2-phenylindoleninone as a red solid unstable to water or base, while Neunhoeffer[3] claimed the isolation from aqueous sodium hydroxide of both 2-phenyl- and 2-methylindoleninone as yellow stable materials.

The preparation of Neunhoeffer's "2-methylindoleninone," m.p. 174°, was repeated but the product, m.p. 174°, showed strong N–H absorption at 3400 cm.$^{-1}$ and carbonyl absorption at 1680 cm.$^{-1}$. The ultraviolet spectrum of the product displayed peaks at 395, 255, and 235 mμ characteristic of 2,2-disubstituted indoxyls.[6] The n.m.r. spectrum of the product in deuterated dimethylsulfoxide showed a singlet at 8.52 τ (isolated CH_3) and a weak singlet at 6.74 τ (NH) which shifted on addition of acetic acid. Molecular weight determination (289 ± 30; calcd. 292) confirmed a dimeric structure such as 2,2'-dimethyl-2,2'-diindoxyl (VI). Reduction of diindoxyl VI with sodium borohydride yielded 2-methyl-3-hydroxyindoline (VIII) which gave a positive ferric chloride test. Molecular weight determination showed VIII to be a monomer and this fact was confirmed by n.m.r. A possible path for cleavage of VI on hydride reduction is indicated by dotted arrows. Acidification of hydroxyindoline VIII yielded authentic 2-methylindole.

When the preparation of "2-phenylindoleninone" from ethyl α-(2-carbethoxyanilino)-α-phenylacetate (IX) was repeated according to Neunhoeffer and Lehmann,[3] the product obtained was 2,2'-diphenyl-2,2'-diindoxyl (VII), m.p. 180–181°, rather than 2-phenylindoleninone, m.p. 102°. Kalb and Bayer[5] had observed that 2-phenylindoleninone (III) reacts readily with 2-phenylindoxyl (X) in basic solution to yield a dimer, m.p. 180°, for which they favored structure XI over VII. Both VI and VII were prepared by analogous methods and showed similar infrared and ultraviolet absorptions. This and the fact that diindoxyl VII lacked absorption characteristic of an indole chromophore at 280–290 mμ, render structure XI improbable.



The primary product expected from ring closure of diester IX followed by decarboxylation is 2-phenylin-

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[1] Parke, Davis Research Fellow 1961–1962.

[2] *Cf.* P. L. Julian, E. W. Meyer, and H. C. Printy, "Heterocyclic Compounds," Vol. III, R. C. Elderfield, ed., J. Wiley and Sons, New York, N. Y., 1952.

[3] O. Neunhoeffer and G. Lehmann, *Ber.*, **94**, 2960 (1961).

[4] A. Hassner and M. J. Haddadin, *Tetrahedron Letters*, No. **21**, 975 (1962).

[5] L. Kalb and J. Bayer, *Ber.*, **45**, 2150 (1912).

[6] B. Witkop and J. B. Patrick, *J. Am. Chem. Soc.*, **73**, 2188 (1951).