Acknowledgment.—This work was supported in part by a grant from the Research Corporation. We wish to express our thanks to Dr. John E. Campion of Riker Laboratories, Inc., for his interest in this work and to the Analytical Division of Riker Laboratories for nitrogen and halogen analyses and spectra.

Organotin Chemistry. III.[1] Dibutyltin Diphenoxide

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Dialkyltin diphenoxides have been mentioned in the literature[2] but there are no details of the synthesis or characterization of a member of this class of materials. We prepared dibutyltin diphenoxide (I) by the action of sodium phenoxide on dibutyltin dichloride in heptane (1). The product is extremely sensitive to adventitious moisture and in order to prepare it, extreme care to exclude the atmosphere had to be exercised.

$$(n\text{-}C_4H_9)_2SnCl_2 + 2C_6H_5O^{\ominus}, Na^{\oplus} \longrightarrow (n\text{-}C_4H_9)_2Sn(OC_6H_5)_2 + 2NaCl \quad (1)$$

The diphenoxide I was hydrolyzed by water (2) to give tetrabutyl-1,3-diphenoxydistannoxane II in 95% yield. II was also prepared by the reaction of dibutyltin oxide and I (3). The distannoxane II exist as a dimer.[1]

$$4Bu_2Sn(OC_6H_5)_2 \xrightarrow{H_2O} \underset{\text{II}}{\{[(n\text{-}C_4H_9)_2SnOC_6H_5]_2O\}_2} \quad (2)$$

$$2Bu_2Sn(OC_6H_5)_2 + 2Bu_2SnO \longrightarrow \text{II} \quad (3)$$

Experimental[3]

Dibutyltin Diphenoxide (I).—Sodium metal (46.0 g., 2 g.-atoms) was dissolved, during stirring, in 1 l. of absolute methanol contained in a three-necked flask provided with a nitrogen atmosphere, a drying tube, and a reflux condenser, with a Dean–Stark apparatus and mechanical stirring. To the freshly prepared solution of sodium methoxide, phenol (188.2 g., 2 moles) was added and the reaction mixture was refluxed for 2 hr. One liter of anhydrous heptane was then added and the methanol was removed by azeotropic distillation, and separation, in the Dean–Stark apparatus. Complete removal of methanol took some 18 hr. of reflux. Replenishment of the heptane lost by its solubility in methanol was made by periodic additions. As the stripping proceeded, a white solid, (sodium phenoxide) precipitated.

During stirring, a solution of dibutyltin dichloride (303.8 g., 1 mole) was added and the reaction mixture refluxed for 4 hr. The mass was then allowed to cool and the solids (NaCl) separated by vacuum filtration on a Büchner funnel, under a blanket of nitrogen; they were washed with 250 ml. of anhydrous heptane and air dried. These solids weighed 121.7 g. (104%, 2.08 moles).

The filtrate and heptane wash were combined and the heptane removed by vacuum distillation to give an orange oil which crystallized on cooling; yield 379.8 g. (90%; 0.90 mole). The crude yield was divided into two portions and characterized separately by both recrystallization and distillation.

Repeated recrystallizations from anhydrous pentane gave white crystals with a constant m.p. of 45–48° (sealed capillary).

Anal. Calcd. for $C_{20}H_{28}SnO_2$:Sn, 28.32; mol. wt., 419.12. Found: Sn, 28.47; mol. wt. (Thermistor Osmometer), 415.

Repeated vacuum distillations of a portion of the crude gave white crystalline material; b.p. 161°/0.35 mm.

Anal. Calcd. for $C_{20}H_{28}SnO_2$: Sn, 28.32. Found: Sn, 28.42. The infrared spectra of the two materials were identical.

Carbon and hydrogen analyses gave erratic results which were ascribed to hydrolysis by adventitious moisture during shipping and handling. Attempts to titrate the material with alkali gave very poor end points. Therefore, a quantitative saponification was done in order to provide a second reliable analytical determination. The sample was saponified with alcoholic potassium hydroxide and the dibutyltin oxide isolated, washed with acetone, dried, and weighed. The results are expressed as % dibutyltin oxide (% Bu_2SnO). For the material purified by recrystallization:

Anal. Calcd. for $C_{20}H_{28}SnO_2$: % Bu_2SnO, 59.39. Found: % Bu_2SnO, 58.72.

For the material purified by distillation:

Anal. Calcd. for $C_{20}H_{28}SnO_2$: % Bu_2SnO, 59.39. Found: % Bu_2SnO, 58.28.

Hydrolysis of Dibutyltin Diphenoxide.—Dibutyltin diphenoxide (4.19 g., 10 mmoles) was stirred for 2 hr. with 100 ml. of water. The white solid was isolated by filtration, washed with water, pressed dry, and dried over phosphorus pentoxide *in vacuo;* yield 3.17 g. (2.4 mmoles, 95%). Recrystallization from hexane gave tetrabutyl-1,3-diphenoxydistannoxane; m.p. 137–139° (lit.[1] 137–139.5°), undepressed when mixed with authentic material. The infrared spectra and X-ray powder patterns were identical with those of an authentic sample.

Reaction of Dibutyltin Diphenoxide with Dibutyltin Oxide.—Dibutyltin oxide (6.23 g., 25 mmoles) was added to a solution of dibutyltin diphenoxide (10.48 g., 25 mmoles) in 125 ml. of anhydrous benzene. During stirring, the mixture was heated to boiling to achieve complete solution. The only slightly hazy solution was filtered while hot and the benzene removed by vacuum distillation.

A white crystalline solid was obtained in 99% yield (16.5 g., 12 mmoles). After one recrystallization from hexane, the melting point was 137–139.5° (lit.,[1] 137–139.5); it was undepressed when mixed with authentic material. The infrared spectra and X-ray powder patterns were identical with those of an authentic sample of tetrabutyl-1,3-diphenoxydistannoxane.

Acknowledgment.—The analyses were performed by Mr. H. Corbin and his associates with the exception of the C,H determinations which were done by Spang Microanalytical Laboratory, Ann Arbor, Michigan. The molecular weights and spectra were determined by Mr. I. Simmons and his associates.

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[1] Paper II, Wm. J. Considine, J. J. Ventura, A. J. Gibbons, Jr., and A. Ross, *Can. J. Chem.*, in press.

[2] See R. Ingham, S. Rosenberg, and H. Gilman, *Chem. Rev.*, **60**, 459 (1960).

[3] All melting points are uncorrected.

Photodimerization of a Pseudoxazolone[1,2]

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Pseudoxazolones [(5-[2H]oxazolones)] have been postulated by Bergmann[3] as intermediates in the formation of 5-[4H]oxazolones from N-(α-haloacyl)amino acids. A few pseudoxazolones have been isolated, of which only 2-benzylidene-4-methylpseudoxazolone (I) has received much attention. Ring closure of N-(α-chlorophenylacetyl)alanine (II) gives compound I, for which a

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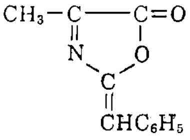
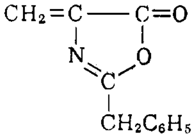
[1] This work was supported by a research grant from the National Science Foundation (G-9985).

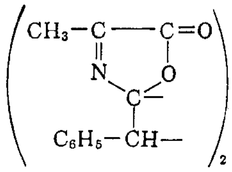
[2] Abstracted, in part, from the Ph.D. thesis of E. J. Piasek, Illinois Institute of Technology, June, 1962.

[3] M. Bergmann and F. Stern, *Ann.*, **448**, 20 (1926).

variety of melting points (106–109°,[4] 122–123°,[5] and 155–170°[6]) have been reported. This variability might be due to the presence of the tautomeric 5-[4H]oxazolone (III), although geometric isomerism about the exocyclic double bond has been suggested.[7] Our research was, therefore, directed toward clarifying this point.


I


III


IV

When compound II was treated with acetic anhydride in pyridine, a yellow solid, melting range 109–125°, was obtained. Compound I, m.p. 109–111°, was isolated from this material by sublimation. The intense infrared absorption at 1785 cm.$^{-1}$ is due to the lactone carbonyl group. The ultraviolet maxima at 240 mμ (ε 8640) and at 356 mμ (ε 33,200) are also consistent with the structure of I ($C_6H_5CH = C<$[8] and $C_6H_5CH{=}C{-}N{=}C{-}C{=}O$ chromophores, respectively).

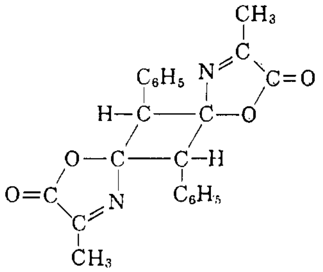
A white material (IV) remained after sublimation of I. Crystallization from a solution of methylcyclohexane and chloroform gave a substance, m.p. 209–210°, whose elemental analysis and molecular weight indicated that it was a dimer. On standing in ordinary light for several days, I developed a white crust, which was shown to be this dimer. Moreover, when I was irradiated with sunlight or ultraviolet light, the rate of dimer formation was markedly enhanced. That the dimerization is light-catalyzed was further substantiated by the absence of IV after a freshly prepared sample of I was placed in an opaque container.

In contrast to I, compound IV exhibited only end absorption in the ultraviolet, but possessed infrared bands at 1785 cm.$^{-1}$ and 1650 cm.$^{-1}$ ($>C{=}N$). The absence of ultraviolet absorption indicated that the chain of conjugation had been broken, presumably at the styryl moiety. The infrared spectrum suggested that the conjugation of the α,β-unsaturated carbonyl system remained intact, for the carbonyl group of the dimer absorbed at the same frequency as did the monomer.

Of several possibilities, only a cyclobutane structure for IV was in reasonable accord with the spectral data. The proton magnetic resonance spectrum of the dimer gave further support for this structure, since three kinds of hydrogen were found at τ = 2.6, 4.97, and 7.64. The broad band at 2.6 is attributed to the aromatic protons.[9] The bands at 4.97 and 7.64 appeared as sharp singlets in the intensity ratio of 1:3. The latter band may be assigned to the protons of a methyl group which is α to the double bond of an oxazole ring (τ = 7.60[10]), while the former is in agreement with values of 5–6 observed for highly deshielded protons of a substituted cyclobutane ring.[11,12]

The formation of cyclobutane compounds by photodimerization of conjugated carbonyl systems is well established.[11,13–15] Of special interest is the dimerization of benzylidene phthalide.[16] This dimer is so similar to IV that its formation provides supportive analogy for the proposed cyclobutane structure.

The n.m.r. spectrum does not supply sufficient evidence to allow a choice of stereoisomers of IV. However, the lack of line splitting militates against structures in which the cyclobutane ring protons are nonequivalent. One is tempted to favor a structure V, in which the monomers have added in a head to tail arrangement so as to place the phenyl groups *trans* to one another. However, it is recognized that in solid-state reactions, crystal geometry is an important consideration in determining the stereochemistry of the product.


V

Experimental[17]

2-Benzylidene-4-methylpseudoxazolone (I).—Twenty grams (0.083 mole) of N-(α-chlorophenylacetyl)alanine[5] was added to a solution of 60 ml. of pyridine (dried over potassium hydroxide) in 300 ml. of acetic anhydride. After 30 min., the contents were poured over 500 g. of ice, the mixture was stirred well, and the light yellow solid thus obtained was dried *in vacuo* for several days to give 13.8 g. (84.2%) of pseudoxazolone, m.p. 109–120° (reported m.p. 105–115[5]). This material was sublimed at 68° (1 mm.) to yield a yellow solid, m.p. 109–111°, λ_{max}^{EtOH} 240 (ε 8640) and 356 mμ (ε 33,200); $\nu_{max}^{CH_2Cl_2}$ 1785, 1680, and 1660 cm.$^{-1}$. Further sublimations failed to improve the melting point.

Anal. Calcd. for $C_{11}H_9NO_2$: C, 70.58; H, 4.84; N, 7.48; mol. wt., 187. Found: C, 70.58; H, 5.08; N, 7.68; mol. wt. (Rast), 187.

Photodimer (IV).—Dry, freshly prepared pseudoxazolone (1.48 g.) was placed in a vacuum desiccator and after 1 week a white solid had formed on its surface. The solid was sublimed at 80° (1 mm.) until only 37 mg. (2.5%) of white residue, m.p. 130–210°, remained. Crystallization of this solid was difficult to achieve, but the following procedure proved to be adequate: The crude product was dissolved in chloroform and methylcyclohexane was added so as to induce cloudiness. The satu-

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[4] H. T. Clarke, J. R. Robinson, and R. Robinson, "The Chemistry of Penicillin," Princeton University Press, Princeton, N. J., 1949, p. 793.

[5] J. A. King and F. M. McMillan, *J. Am. Chem. Soc.*, **72**, 833 (1950).

[6] M. Brenner and K. Rufenacht, *Helv. Chim. Acta*, **37**, 203 (1954).

[7] R. C. Elderfield, "Heterocyclic Compounds," Vol. 5, John Wiley and Sons, Inc., New York, N. Y., 1957, p. 375.

[8] D. A. Bassi, V. Deulofeu, and A. F. Ortega, *J. Am. Chem. Soc.*, **75**, 171 1953).

[9] H. Conroy, "Advances in Organic Chemistry," Vol. II, Interscience Publishers, Inc., New York, N.Y., 1960, p. 291.

[10] P. Yates and E. S. Hand, *Tetrahedron Letters*, No. **19**, 669 (1961).

[11] G. W. Griffin, A. F. Vellturo, and K. Furukawa, *J. Am. Chem. Soc.*, **83**, 2725 (1961).

[12] J. Corse, M. J. Finkle, and R. E. Lundin, *Tetrahedron Letters*, No. **1**, 1 (1961).

[13] A. Mustafa, *Chem. Revs.*, **51**, 1 (1952).

[14] E. C. Taylor and W. W. Paudler, *Tetrahedron Letters*, No. **25**, 1 (1960).

[15] R. Anet, *Chem. Ind.* (London), 897 (1960).

[16] A. Schönberg, N. Latif, R. Moubasher, and W. I. Awad, *J. Chem. Soc.*, 374 (1950).

[17] Melting points were determined on a Fisher-Johns block and are uncorrected.

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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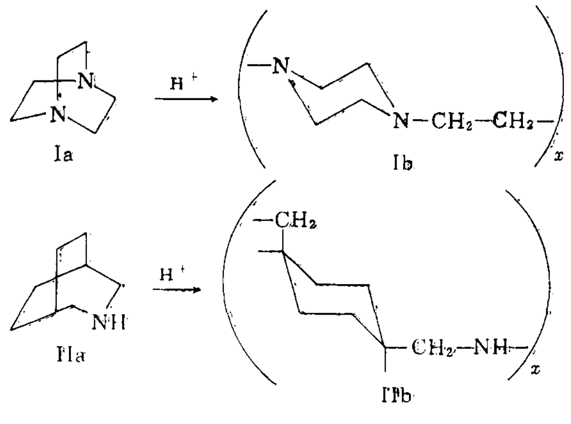
Relatively few ring-opening polymerizations of cyclic amines have been described. Ethylenimine polymerizes very readily[1] as would be expected for a highly strained ring. Pyrrolidine, piperidine, and hexamethylenimine were reported by Friederich[2] to give low polymers when heated with acid. Cope and 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:

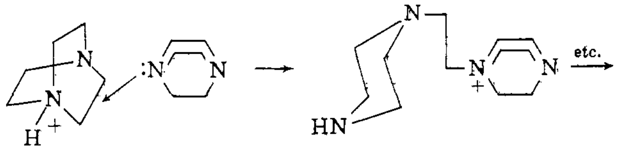


This proved to be the case.

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.