zwitterionic form IV, known to contribute appreciably to the structure of negatively substituted ketenimines.[5a,b]

Dicyanoketenimine is completely ionized in aqueous[6] or aquoethereal solutions as judged by ultraviolet[6] and infrared spectra. In the form of hydronium tricyanomethanide it is reasonably stable, since the addition of water proceeds slowly.[7] On dehydration, however, dicyanoketenimine is obtained instead of tricyanomethane. This fact is not too surprising, as it is known that negatively substituted malononitriles exist as the 1,1-dicyanoethylene tautomers,[8] probably favored on account of their resonance stabilization through structures analogous to IV, impossible in substituted dicyanomethanes. By the analogy between the $(NC)_2C{=}C\langle$ and $O{=}C\langle$ groups,[9] tricyanomethane and dicyanoketenimine are cyanocarbon analogs of cyanic and isocyanic acid. In fact, addition reactions of "cyanoform" resemble closely those of isocyanic acid, as does its facile autoaddition–polymerization. The dicyanoketenimine structure accounts readily for all these properties.

Experimental

Aquoethereal "Cyanoform."—This solution was prepared from potassium tricyanomethanide[7] as previously described.[1a,b] According to Hantzsch and Oswald,[1b] the composition is cyanoform–water–ether in 1:10:10 ratio. A nuclear magnetic resonance spectrum of this solution had, apart from the ethyl peaks (triplet and quadruplet centered at $\tau = 9.04$ and $\tau = 6.70$, respectively), a single proton peak at $\tau = 4.00$. The relative intensities of these peaks supported the earlier analysis.[1b]

The infrared spectrum of the aqueoethereal solution was characterized by tricyanomethanide bands at 4.61, 7.97, and 8.03 μ.[10]

Dicyanoketenimine.[11]—Five milliliters of aquoethereal "cyanoform" was placed on a watch glass and evaporated rapidly by directing a stream of air over the surface until a thick slurry was obtained. It was filtered immediately and the yellowish crystals pressed dry; yield 150–160 mg. Sublimation of this material at 1 mm. starting at a bath temperature of 60° and slowly raising it to 90° gave about 70 mg. of white crystals. The sublimate has no melting point but starts turning orange at 70° and decomposes to a red tar around 140°.

Anal. Calcd. for C_4HN_3: C, 52.7; H, 1.11; N, 46.1. Found: C, 52.2; H, 1.45; N, 45.6.

The infrared spectrum (Nujol mull) is characterized by bands at 4.0, 4.4, 4.55, 5.6, 7.98, 9.76, and 12.16 μ and is not significantly different from that of the crude solid.

A sample of the sublimate was dissolved in water and a portion of the solution was treated with aqueous silver nitrate. Silver tricyanomethanide precipitated immediately and was identified by its infrared spectrum.

Another portion of the solution was treated with excess *t*-butylamine yielding, on concentration of the solution, *t*-butylammonium tricyanomethanide, identified by comparison with authentic material[7] (mixed melting point and superimposition of infrared spectra).

Treatment of sublimed dicyanoketenimine with excess ethanol afforded, on evaporation of the solution, a solid identified as 1-amino-1-ethoxy-2,2-dicyanoethylene by comparison with authentic material[9] (mixed melting point and superimposition of infrared spectra).

(5) (a) R. K. Bullough and P. J. Wheatley, *Acta Cryst.*, **10**, 233 (1957); (b) Dinitroacetonitrile [C. O. Parker, W. D. Emmons, H. A. Rolewicz, and K. S. McCallum, *Tetrahedron*, **17**, 79 (1962)], which may be regarded as dinitroketenimine exhibits properties that parallel those of cyanoform. It could not be isolated in anhydrous state and infrared data are, consequently, lacking.

(6) R. H. Boyd, *J. Am. Chem. Soc.*, **83**, 4288 (1961).

(7) S. Trofimenko, T. L. Little, and H. F. Mower, *J. Org. Chem.*, **27**, 433 (1962).

(8) F. Arndt, H. Scholz, and E. Frobel, *Ann.*, **521**, 95 (1935).

(9) W. J. Middleton and V. A. Engelhardt, *J. Am. Chem. Soc.*, **80**, 2788 (1958).

(10) F. A. Miller and W. K. Baer of Mellon Institute obtained values of 4.60 and 8.05 μ in aqueous solution and 4.60, 7.99, and 8.07 μ in the solid (private communication).

(11) Note: This procedure was found to be most convenient for preparing small samples of dicyanoketenimine. All of the operations must be conducted rapidly, as crude dicyanoketenimine and its concentrated solutions are unstable. Scaling up was not feasible as larger samples were much more prone to polymerize.

Nucleophilic Substitution at the Pyridazine Ring Carbons. I. Synthesis of Iodopyridazines

PETER COAD, RAYLENE ADAMS COAD, SHARON CLOUGH,[1] JUNE HYEPOCK, ROLLAND SALISBURY, AND CHARLES WILKINS[1]

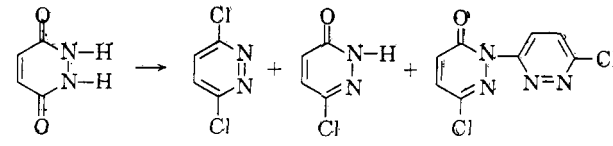
Department of Chemistry, Chapman College, Orange, California

Received August 17, 1962

In recent years interest has grown in the chemistry of the substituted pyridazines because of the theoretical aspects of the pyridazine ring system[2,3] and because of biological activity shown by many of these compounds.[4,5] A study of structure-reactivity correlations of substituted pyridazines is being conducted in this laboratory. A general procedure was sought by which satisfactory yields of iodopyridazines could be obtained from readily available starting materials. Previously, Horning and Amstutz[6] reported that substituted iodopyridazines might be formed as by-products in the reduction of highly substituted chloropyridazines with red phosphorus and hydriodic acid.

The route which appeared attractive was the nucleophilic substitution at the ring carbons using chloro- or bromopyridazines as the substrate and iodide ion as the nucleophile since chloro- and bromopyridazines can be prepared by one- or two-step syntheses from commercially available starting materials. For example, maleic hydrazide (I) can be converted to chloro or bromo compounds.

In spite of the fact that the synthesis of 3,6-dichloropyridazine (II) using phosphorus oxychloride is described several times in the literature,[7,8] Feuer and Rubenstein[9] showed by meticulous work that the product from such reactions is contaminated with 3-chloro-6-hydroxypyridazine (III) and to a lesser extent with 1-(3′-chloro-6′-pyridazyl)-3-chloro-6-pyridazone (IV). The over-all yield of pure dichloropyridazine was of the order of 30%. Difficulties in obtaining dichloropyridazine of high purity were also encountered



I II III IV

(1) Participants in Undergraduate Research Training Grant NSFG11835 from the National Science Foundation.

(2) S. F. Mason, *J. Chem. Soc.*, 674 (1958).

(3) S. F. Mason, *ibid.*, 1240 (1959).

(4) J. Druey, Kd. Meier, and K. Eichenberger, *Helv. Chim. Acta*, **37**, 121 (1954).

(5) J. Druey, U.S. Patent 2,764,584 (1956).

(6) R. H. Horning and E. D. Amstutz, *J. Org. Chem.*, **20**, 707 (1955).

(7) R. H. Mizzoni and P. E. Spoerri, *J. Am. Chem. Soc.*, **73**, 1873 (1951).

(8) M. M. Rogers and J. P. English, U.S. Patent 2,671,086 (1954).

(9) H. Feuer and H. Rubenstein, *J. Org. Chem.*, **24**, 811 (1959).

in this laboratory and it was found that the recrystallization and sublimation process used by Feuer and Rubenstein was difficult and time-consuming since both dichloropyridazine and 3-chloro-6-hydroxypyridazine were recrystallized from the same solvent and both underwent sublimation. Separation of the compounds by vacuum distillation was also inconvenient because of the high melting points of the solids to be collected as distillates. (Dichloropyridazine melts at 66–68° and chlorohydroxypyridazine at 139–140°.) These two compounds have been found in this laboratory to interact under such conditions. Consequently, a method was sought to produce a maximum yield of dichloropyridazine which would be uncontaminated by the pyridazone. Actually, the problem became one of finding correct experimental conditions to minimize the hydrolysis of dichloropyridazine that normally occurs during the neutralization procedure required in the isolation of dichloropyridazine from the crude reaction mixture and to remove any small quantities of III and IV that might be formed. The specific experimental procedure is the result of over two hundred runs to find optimum conditions.[10]

It will be noted that the reaction mixture is triturated by adding small portions to dilute ammonium hydroxide at 0°. This prevents any local heating and consequent hydrolysis of dichloropyridazine. Any traces of III and IV are removed during the cold sodium hydroxide trituration step. Compound III is soluble in 1 *N* sodium hydroxide. Although 3,6-dichloropyridazine reacts rapidly with warm aqueous sodium hydroxide to produce III,[11] the rate of the reaction is very small at 0° or less.

This same type of procedure using triturations in cold ammonium hydroxide and sodium hydroxide has also been used to prepare 3,6-dibromopyridazine, 4 - methyl - 3,6 - dichloropyridazine, 4 - methyl - 3,6-dibromopyridazine, 3,4,6 - trichloropyridazine, and 3,4,5,6 - tetrachloropyridazine in high purity. Therefore, a general procedure for preparation of pure chloro- and bromopyridazines, in which the formation of pyridazones by inadvertant hydrolysis is minimized, has been elucidated and should prove of value for synthetic and theoretical work for which pure compounds are required.

In the preparation of iodopyridazines three different reaction media were used. The first method utilized 50% hydriodic acid with heating under reflux. This took advantage of the solubility of the halopyridazines in acid and a large excess of iodide ion. Bruce and Perez-Medina[12] observed that 2-methyl-3-nitro-4,6-dichloro-5-cyanopyridine was converted to 2-methyl-3-nitro-4,6-diiodo-5-cyanopyridine during an attempted reduction of the nitro group with hydriodic acid and it was thus thought possible that chloro- or bromopyridazines might undergo halogen exchange with hydriodic acid under reflux. This method can, indeed, be used to synthesize iodopyridazines, but there was difficulty in isolation of the products and the yields were not high.

(10) Trials performed by participants in Summer Science Training Program (1961) and Coöperative College–School Program (1962) sponsored by the National Science Foundation.

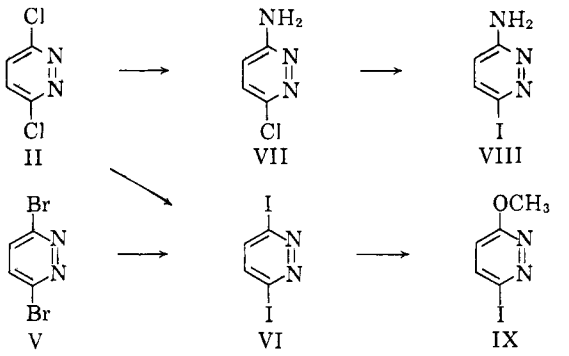
(11) S. Du Breuil, *J. Org. Chem.*, **26**, 3382 (1961).

(12) W. F. Bruce and L. A. Perez-Medina, *J. Am. Chem. Soc.*, **69**, 2571 (1947).

The second method involved the use of acetone with a stoichiometric amount of hydriodic acid. Investigation showed that the driving force behind this reaction was the formation of the insoluble hydroiodide salts of iodopyridazines in this media. The method proved useful for bromopyridazines, but not for chloropyridazines.

The third method, which proved to be superior in nearly all instances, consisted of combining anhydrous acetone solutions of the chloro- or bromopyridazine and sodium iodide with a catalytic amount of hydriodic acid present. This method utilizes the insolubility of sodium bromide and sodium chloride in anhydrous acetone to drive the reaction to completion. The reaction generally will begin without catalysis with bromopyridazines but yields are greatly improved by its use. The chloropyridazines generally fail to react without the addition of hydriodic acid as catalyst. The insoluble sodium halides formed during the course of the reaction provide a convenient method for following the progress of the reaction.

Thus, 3,6-dibromopyridazine (V) and 3,6-dichloropyridazine (II) were converted to 3,6-diiodopyridazine



(VI); 3,6-dichloropyridazine (II) was converted to the hydroiodide of 3-amino-6-iodopyridazine (VIII) by way of 3-amino-6-chloropyridazine (VII); and 3,6-diiodopyridazine was converted to 3-methoxy-6-iodopyridazine (IX).

Experimental

3,6-Dichloropyridazine.—A mixture of 61 g. (0.5 mole) of maleic hydrazide and 200 ml. of freshly distilled phosphorus oxychloride was placed in a 500-ml. three-necked flask equipped with a mechanical stirrer, thermometer, and reflux condenser connected to a sodium hydroxide trap. The mixture was heated on a water bath so that the internal temperature was held at about 70°. (Higher temperatures lead to formation of black viscous material.) The reaction was continued for 1 hr. after the rapid evolution of hydrogen chloride gas ceased, a total of about 3 hr. The excess phosphorus oxychloride was removed by vacuum distillation using a vacuum pump protected with an acetone–Dry Ice trap and a capillary bleed, pressure about 15 mm. The distillation temperature and pressure were adjusted as necessary so that the temperature of the heating bath was never higher than 80°. The sirupy residue was transferred to a beaker and cooled to − 10°.

A mixture of dilute ammonium hydroxide and chipped ice was prepared with a resulting concentration of about 2 *N*. A portion of this was placed in a cold mortar and to it were carefully added very small portions of the crude product for careful trituration. Two factors were frequently checked during this process, pH and temperature. The pH was kept at 8 or higher and the temperature was never allowed to rise above 0°. If the pH became too low, the contents of the mortar were decanted into a beaker and fresh ammonium hydroxide–ice mixture was added to the mortar. If the temperature started to rise, more ice was added.

This process of triturating very small portions of the product, so small that local heating effects were eliminated, was continued until all of the material had been triturated at pH 8–11 at 0°. The solid was isolated by filtration and rapidly triturated with 100 ml. of cold (0° or less) 1 *N* sodium hydroxide followed by washing with distilled water to pH 7. The crude dichloropyridazine was air dried, 45 g. (60%) and then continuously extracted with petroleum ether (30–60°) to form pure dichloropyridazine, 28.6 g., white needles, m.p. 68–69° (lit.,[7] 68–69°).

3,6-Dibromopyridazine.—A mixture of 100 g. of maleic hydrazide (0.9 mole) and 431 g. (1 mole) of phosphorus pentabromide (prepared by very slow dropwise addition of bromine to phosphorus tribromide or to red phosphorus in a polyethylene flask or in a polyethylene beaker with an inverted glass funnel of appropriate size taped to the top of the beaker) was carefully triturated for 5 min. in a mortar and was quickly transferred to a polyethylene flask equipped with a reflux condenser. The flask was placed in a deep bath of boiling water and heated until evolution of white fumes of hydrogen bromide ceased, approximately 3 hr. The resulting orange solid was triturated as described for dichloropyridazine. The crude 3,6-dibromopyridazine was air dried, 104 g. (49%), and then continuously extracted with ligroin (60–70°) to form 71 g. of pure dibromopyridazine, silky white needles, m.p. 115–116° (lit.,[13] 115–116°).

4-Methyl-3,6-dichloropyridazine.—A mixture of 50 g. (0.4 mole) of citraconic hydrazide and 200 ml. (2.20 moles) of phosphorus oxychloride was stirred and heated as described for dichloropyridazine, triturated in the same manner to obtain 38.5 g. (60%), and then continuously extracted with ligroin (60–70°) to form 31 g. pure 4-methyl-3,6-dichloropyridazine, m.p. 83–84° (lit.,[14] 83.5–84°).

3,4,6-Trichloropyridazine.—Twenty grams (0.13 mole) of 4-chloro-3,6-dihydroxypyridazine prepared by the method of Mizzoni and Spoerri[14] and 75 ml. of phosphorus oxychloride were placed in a 250-ml. Erlenmeyer and heated under reflux in a boiling water bath for 1 hr. after complete solution occurred. The product was isolated in the new manner, dried in a vacuum dessicator, and extracted with petroleum ether to give 8.7 g. (30%) pure 3,4,6-trichloropyridazine, white needles, m.p. 57–58 (lit.,[14] 57–57.5°).

3,4,5,6-Tetrachloropyridazine.—Forty grams of 4,5-dichloro-3,6-dihydroxypyridazine prepared by the process of Pennino[15] was mixed with 150 ml. of phosphorus oxychloride and heated under reflux on a hot plate for 1 hr. after evolution of hydrogen chloride had ceased. Product was isolated as above to give 22 g. (46%) pure 3,4,5,6-tetrachloropyridazine, m.p. 85–86° (lit.[15] 85–86°).

4-Methyl-3,6-dibromopyridazine. Method A.—A mixture of 431 g. (0.1 mole) of phosphorus pentabromide and 84 g. (0.67 mole) of citraconic hydrazide was triturated in a mortar and transferred to a polyethylene flask equipped with a reflux condenser. The mixture was heated in a deep bath of boiling water for 8 hr., and it was then triturated and washed in the usual manner. The precipitate was thoroughly dried in air and in a vacuum oven to constant weight and extracted in a Soxhlet extractor with petroleum ether to give 68.6 g. (42%), white needles, m.p. 104–105°; λ_{max}^{EtOH} 276 mμ, ε 1240.

Anal. Calcd. for $C_5H_4Br_2N_2$: C, 23.81; H, 1.59; Br, 63.49; N, 11.11. Found: C, 24.44; H, 1.32; Br, 61.58; N, 10.89.

Method B.—A mixture of 8.3 g. (0.015 mole) of phosphorus pentabromide and 1.1 g. (0.008 mole) of 5-methyl-3-chloro-6-pyridazone prepared by the method of Linholter, *et al.*,[16] was thoroughly triturated and then heated under reflux on a boiling water bath for 0.5 hr. The mixture was cooled and 15 ml. of ice–water was added in small portions with stirring. The precipitate was collected and recrystallized from ethanol to give 0.4 g. (21%) white crystals, m.p. 104–105°.

Anal. Calcd. for $C_5H_4Br_2N_2$:C, 23.81; H, 1.59; Br, 63.49; N, 11.11. Found: C, 24.03; H, 1.62; Br, 63.68; N, 11.03.

3,6-Diiodopyridazine.—Three methods were developed using 3,6-dibromopyridazine as the starting material.

Method A.—A mixture of 1 g. (0.004 mole) of 3,6-dibromopyridazine and 8.5 ml. (excess) of 50% hydriodic acid was heated under reflux in an oil bath at 130° for 2 hr. The solid was removed by filtration, triturated with cold water, filtered, and dried. The crude solid was recrystallized using methanol–water, 0.4 g. (30%), white crystals, m.p. 157–158°; λ_{max}^{EtOH} 247 mμ, ε 14680.

Anal. Calcd. for $C_4H_2I_2N_2$: C, 14.76; H, 0.63; I, 76.19; N, 8.43. Found: C, 14.71; H, 0.67; I, 76.42; N, 8.29.

Method B.—To a solution of 10 ml. of 50% hydriodic acid dissolved in 25 ml. of acetone heated under reflux was added dropwise 8 g. of 3,6-dibromopyridazine dissolved in 25 ml. of acetone. The mixture was heated under reflux for 15 min. and the bright yellow solid was removed by filtration, 6.38 g., m.p. 171.5–172°. When this solid, the hydroiodide salt of 3,6-diiodopyridazine, was thoroughly triturated with 50 ml. of water, a pale yellow precipitate of 3,6-diiodopyridazine formed, 4.57 g. (41.3%), m.p. 162–163°, a portion of which was rewashed and crystallized from acetone–water, m.p. 157–158°.

Method C.—To a solution of 30 g. (0.2 mole) of sodium iodide dissolved in 150 ml. of dry acetone heated under reflux was added, dropwise with magnetic stirring over a 15-min. period, 23.8 g. (0.1 mole) of dibromopyridazine dissolved in 150 ml. of dry acetone. The reaction was heated and stirred under reflux for 0.5 hr. At the end of this period 2 drops of 50% hydriodic acid dissolved in 5 ml. of acetone were added. The same addition was repeated at half-hour intervals until three portions had been added. Heating was continued for 0.5 hr. after the last addition. The sodium bromide which formed was filtered from the solution and weighed (19.0 g.). An additional 5-ml. portion of the hydriodic acid–acetone solution was added to the filtrate and heated for another half-hour to confirm that the reaction was completed. By concentrating the acetone solution and crystallization there was obtained 25.2 g. (74%) of light tan flaky material, a portion of which was continuously extracted with petroleum ether to give white crystals, m.p. 157–158°.

Two methods were developed using **3,6-dichloropyridazine** as starting material.

Method A.—A mixture of 8.5 g. (0.057 mole) of 3,6-dichloropyridazine and 86 ml. of hydriodic acid was heated in an oil bath for 1 hr. at 150°. The solid was filtered from the solution and recrystallized three times from a mixed solvent of methanol–water to give white crystals, 10.7 g. (56%), m.p. 157–158°.

Method B.—To a solution of 30 g. (0.2 mole of sodium iodide) and 4 drops of 50% hydriodic acid dissolved in 150 ml. of acetone heated under reflux was added, dropwise with magnetic stirring over a period of 10 min., 14.9 g. (0.1 mole) of dichloropyridazine dissolved in 50 ml. of acetone. Two more portions of hydriodic acid–acetone solution were added at half-hour intervals as the mixture was heated under reflux for 2 hr. The precipitate of inorganic salt was removed by filtration, 4.58 g. A solution of 6 g. of sodium iodide, 4 drops of hydriodic acid, and 50 ml. of acetone was added and the solution was heated with stirring for 30 min. The inorganic salt (0.67 g.) was removed by filtration and the filtrate was concentrated to one-third volume by vacuum distillation and water (*ca.* 50 ml.) was added. Crude 3,6-diiodopyridazine, 25.9 g. (77.5%) of tan solid was obtained, a portion of which was extracted using a Soxhlet extractor and petroleum ether as solvent to give fine white needles, m.p. 157–158°.

3-Iodo-6-aminopyridazine Hydroiodide.—3-Amino-6-chloropyridazine was prepared by the procedure described by Steck, Brundage, and Fletcher.[13] One gram of 3-amino-6-chloropyridazine was heated for 1 hr. on a boiling water bath with an excess of 50% hydriodic acid (8 ml.). The crystals that formed were removed by filtration, washed with ethyl acetate, and dried, 0.18 g., m.p. 197–200° (dec.); λ_{max}^{EtOH} 222 mμ, ε 20750; 349 mμ, ε 19200.

Anal. Calcd. for $C_4H_5I_2N_3$: C, 13.75; H, 1.43; I, 72.78; N, 12.03. Found: C, 13.59; H, 1.45; I, 70.12; N, 11.89.

3-Iodo-6-methoxypyridazine.—To a solution of 0.9 g. (0.04 g.-atoms) of sodium in 50 ml. of dry methanol was added a solution of 11 g. (0.03 mole) of 3,6-diiodopyridazine in 200 ml. of methyl alcohol and allowed to stand overnight at room temperature. The solvent was removed at reduced pressure and the residue was dissolved in 50 ml. of ether, washed with two 10-ml. portions of water, and dried over anhydrous sodium sulfate. The ether was evaporated and the resulting solid was recrystallized from ligroin (66–75) to give 4.5 g. (58%) of flat white needles, m.p. 104–105°, λ_{max}^{EtOH} 226 mμ ε 13300; 290 mμ ε 1610.

Anal. Calcd. for $C_5H_5IN_2O$: I, 53.75; N, 11.87. Found: I, 52.47; N, 11.63.

(13) E. A. Steck, R. P. Brundage, and L. T. Fletcher, *J. Am. Chem. Soc.*, **76**, 3225 (1954).

(14) R. H. Mizzoni and P. E. Spoerri, *ibid.*, **76**, 2201 (1954).

(15) C. J. Pennino, U.S. Patent 2,846,433 (1958).

(16) S. Linholter, A. B. Kristensen, R. Rosenorn, S. E. Nielsen, and H. Kaaber, *Acta Chem. Scand.*, **15**, 1660 (1961).

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

WM. J. CONSIDINE AND J. J. VENTURA

Research Laboratory, Metal and Thermit Corporation, Rahway, New Jersey

Received September 7, 1962

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.

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

The diphenoxide I was hydrolyzed by water (2) to give tetrabutyl-1,3-diphenoxydistannoxane II in 95%

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

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

yield. II was also prepared by the reaction of dibutyltin oxide and I (3). The distannoxane II exist as a dimer.[1]

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.

(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]

ROBERT FILLER AND EDMUND J. PIASEK

Department of Chemistry, Technology Center, Illinois Institute of Technology, Chicago, Illinois

Received July 27, 1962

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

(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).