ized with 2 *N* NaOH. The resulting solid was filtered, washed, and dried to give 1.405 g., 69.2%, of crude product. An analytical sample was obtained from chloroform–*n*-hexane, m.p. 165.5–167°

Anal. Calcd. for $C_{24}H_{23}O_4P$: C, 70.93; H, 5.70; P, 7.62; mol. wt., 406. Found: C, 70.95; H, 5.91; P, 7.69; mol. wt., 379.

The infrared spectra of the esters prepared by the two methods were superimposable and showed two strong carbonyl bands at 1725 and 1610 cm.$^{-1}$.

Reaction of Other Anhydrides with Triphenylphosphine.—Ethereal solutions of equimolar amounts of chloromaleic anhydride and triphenylphosphine were mixed to give a purple precipitate in 94% yield. The infrared spectrum of the crude product showed absorption bands at 1775 and 1705 cm.$^{-1}$ (in mineral oil). Efforts to obtain pure material by recrystallization have been unsuccessful.

When ether solutions of citraconic anhydride (1.12 g.) and triphenylphosphine (261 g.) were mixed, no visible reaction occurred even after refluxing and then allowing the mixture to stand 4 hr. The solvent was removed under vacuum and the tan crystalline mass was allowed to stand overnight. The resulting mixture was deep red and, after washing with ether, gave 1.53 g. of a red, crystalline solid, m.p. 100–103.5° dec. The infrared spectrum (mineral oil) showed a strong band at 1770 cm.$^{-1}$. Unreacted triphenylphosphine (2.05 g.) was recovered from the ether washings.

The Structure of Two New Dibromobenzofurazan Oxides from the Dehydrobromination of Tetrabromotetrahydrobenzofurazan Oxide

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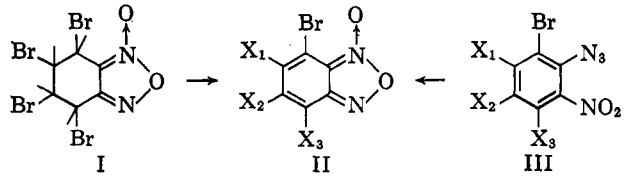
Received June 19, 1964

During an investigation of substituted benzofurazan oxides for fungicidal activity, it was found that treatment of tetrabromotetrahydrobenzofurazan oxide (I) with several nucleophiles yielded two dibromobenzofurazan oxides which had not been described previously.



I II III

a, X_1 = Br, X_2 = X_3 = H
b, X_2 = Br, X_1 = X_3 = H
c, X_3 = Br, X_1 = X_2 = H

Treatment of I with aqueous alkali has been shown to produce a dibromobenzofurazan oxide melting at 132°.[2a] The structure was originally postulated as IIb but was later established as IIc by reduction to the known 3,6-dibromo-*o*-phenylenediamine.[2b]

In the present study, when I, m.p. 169–170°, was treated with pyridine or potassium acetate in glacial acetic acid, a mixture of two new dibromobenzofurazan oxides was formed. One of these had m.p. 148–149° and the other had m.p. 92.5–93°.

The four possible dibromobenzofurazan oxides were synthesized and compared with these two products. The synthesis of IIa, IIb, and IIc was accomplished by ring closure in refluxing toluene of the corresponding azidodibromonitrobenzenes (IIIa, IIIb, and IIIc) which were prepared by diazotization[3] of the corresponding dibromo-*o*-nitroanilines and treatment of the diazonium salts with sodium azide. 5,6-Dibromobenzofurazan oxide was prepared from 4,5-dibromo-2-nitroaniline[4] by oxidation with alkaline hypochlorite.[5]

The products melting at 148–149° and 92.5–93° were found to be identical with synthetic 4,5- and 4,6-dibromobenzofurazan oxide (IIa and IIb), respectively, by mixture melting point and comparison of their infrared spectra. The four dibromobenzofurazan oxides were converted to the corresponding furazans by reduction with hydroxylamine in alkaline solution followed by steam distillation.[6]

The effect of the nucleophile and the solvent on the isomer distribution produced in the dehydrobromination of I is currently under investigation.

Experimental[7]

Preparation of Compounds. Dibromo-*o*-nitroanilines.—5,6-Dibromo-2-nitroaniline was prepared in a four-step reaction sequence: *o*-bromoaniline → 2-bromo-6-nitroaniline[8,9] → 2,3-dibromonitrobenzene[3,10] → 2,3-dibromoaniline[11] → 5,6-dibromo-2-nitroaniline.[12] The last step in the reaction sequence was conducted as follows. 2,3-Dibromoaniline was acetylated to give 2,3-dibromoacetanilide, and 7.0 g. (0.024 mole) of the latter was slowly added with vigorous agitation to 15 ml. of fuming nitric acid (sp. gr. 1.51) at −5°. After 1 hr. at 0° the orange solution was added dropwise to an ice–water mixture to produce a yellow precipitate, which was filtered, washed with water, and recrystallized from 95° ethanol to give 3.27 g. (40%) of 5,6-dibromo-2-nitroacetanilide[12] as fine white needles, m.p. 235–237° dec. A suspension of 4.69 g. (0.014 mole) of the latter in a mixture of 50 ml. of 95% ethanol plus 12 ml. of concentrated hydrochloric acid was refluxed for 48 hr. The suspension was diluted with hot 95% ethanol (*ca.* 30 ml.) to produce a solution which on cooling deposited 3.88 g. (94%) of 5,6-dibromo-2-nitroaniline as yellow needles, m.p. 150.5–151°, lit.[12] m.p. 149°.

4,5-Dibromo-2-nitroaniline was prepared in 75% yield *via* the ethyl nitrate nitration of 3,4-dibromoacetanilide to 4,5-dibromo-2-nitroacetanilide,[4] followed by acid hydrolysis as above, forming orange needles, m.p. 203.5–204.5°, lit.[4] m.p. 204–205°.

4,6-Dibromo-2-nitroaniline was prepared in 84% yield by the bromination of *o*-nitroaniline in glacial acetic acid, forming orange needles, m.p. 127–128° (from 95% ethanol), lit.[13] m.p. 127–128°.

3,6-Dibromo-2-nitroaniline was prepared by Austin's procedure,[14] heating 2,3-dinitro-1,4-dibromobenzene in a sealed tube with ammonia for 3 hr. at 100° and, much more conveniently, by passing ammonia through a suspension of the compound in ethanol. Thus, anhydrous ammonia was bubbled through a suspension of 2.0 g. (6.1 mmoles) of 2,3-dinitro-1,4-dibromoben-

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zene[15,16] in 50 ml. of refluxing absolute ethanol for 3 hr. After 48 hr. at 25° the orange solution was refluxed for an additional 3 hr. while ammonia was passed through. Evaporation gave an orange solid which was chromatographed in benzene on silica gel. A yellow band eluted rapidly and the eluate on evaporation yielded 1.6 g. which on recrystallization from aqueous ethanol gave 1.49 g. (82%) of 3,6-dibromo-2-nitroaniline as yellow needles, m.p. 73.5–74.5°, lit.[14] m.p. 75°.

Azidodibromonitrobenzenes.—The Hodgson and Walker procedure[3] for the diazotization of nitroamines was utilized for the conversion of 5,6-, 4,6-, and 3,6-dibromo-2-nitroaniline to the corresponding diazonium salts. Treatment of the diazonium salts with aqueous sodium azide led to the azidodibromonitrobenzenes. Thus, for the preparation of 1-azido-5,6-dibromo-2-nitrobenzene (IIIa), 1.16 g. (0.017 mole) of finely pulverized sodium nitrite was gradually added to 8 ml. of concentrated sulfuric acid with stirring at 0°. The suspension was heated to 50° and held at this temperature until the sodium nitrite dissolved. The solution was cooled and a finely divided suspension of 3.88 g. (0.013 mole) of 5,6-dibromo-2-nitroaniline in 40 ml. of glacial acetic acid was added gradually with stirring while the temperature was maintained below 15°. After the diazotization was complete, the pale yellow suspension was added dropwise to a solution of 1.16 g. (0.018 mole) of sodium azide in 20 ml. of water with vigorous stirring at 10°. The resulting precipitate was filtered, washed with water, and recrystallized from 95% ethanol. The yield of pale yellow, feathery needles, m.p. 71.5–72.5°, was 3.73 g. (88%).

Anal. Calcd. for $C_6H_2Br_2N_4O_2$: C, 22.38; H, 0.63; Br, 49.65. Found: C, 22.61; H, 0.84; Br, 50.07.

1-Azido-4,6-dibromo-2-nitrobenzene (IIIb) was obtained in 76% yield in the same manner from 4,6-dibromo-2-nitroaniline, forming pale yellow needles from 95% ethanol, m.p. 52–53°.

Anal. Calcd. for $C_6H_2Br_2N_4O_2$: C, 22.38; H, 0.63; N, 17.40. Found: C, 22.65; H, 0.84; N, 17.23.

1-Azido-3,6-dibromo-2-nitrobenzene (IIIc) was obtained in 86% yield from 3,6-dibromo-2-nitroaniline, forming colorless needles from *n*-hexane, m.p. 65.5–66.5°.

Anal. Calcd. for $C_6H_2Br_2N_4O_2$: C, 22.38; H, 0.63; Br, 49.65. Found: C, 22.31; H, 0.71; Br, 49.84.

Dibromobenzofurazan Oxides.—5,6-Dibromobenzofurazan oxide was prepared in 76% yield by the sodium hypochlorite oxidation[5] of 4,5-dibromo-2-nitroaniline, forming yellow needles, m.p. 128–128.5° (from 95% ethanol).

Anal. Calcd. for $C_6H_2Br_2N_2O_2$: C, 24.52; H, 0.69; N, 9.53. Found: C, 24.73; H, 0.75; N, 9.56.

The remaining dibromobenzofurazan oxides were prepared by the thermal decomposition of the corresponding *o*-nitroazides. For example, a solution of 1.0 g. of 1-azido-5,6-dibromo-2-nitrobenzene (IIIa) in 25 ml. of anhydrous toluene was refluxed for 29 hr. Evaporation gave a tan solid. Chromatography in benzene–*n*-hexane (1:1 v./v.) on silica gel gave a yellow band, which eluted readily to yield 4,5-dibromobenzofurazan oxide (IIa), which crystallized from 95% ethanol as pale yellow, feathery needles, m.p. 148–149°. The yield was 0.80 g. (88%).

Anal. Calcd. for $C_6H_2Br_2N_2O_2$: C, 24.52; H, 0.69; N, 9.53. Found: C, 24.57; H, 0.81; N, 9.90.

4,6-Dibromobenzofurazan oxide (IIb) was obtained in 82% yield in the same manner from IIIb, forming canary yellow platelets from 95% ethanol, m.p. 92.5–93°.

Anal. Calcd. for $C_6H_2Br_2N_2O_2$: C, 24.52; H, 0.69; N, 9.53. Found: C, 24.67; H, 0.79; N, 9.65.

4,7-Dibromobenzofurazan oxide (IIc) was obtained in 71% yield from IIIc, forming yellow prisms from 95% ethanol, m.p. 133–133.5.°, lit.[1] m.p. 132°.

Dibromobenzofurazans.—The dibromobenzofurazans were prepared by reduction of the furazan oxides with hydroxylamine followed by steam distillation of the alkaline solution of the dioximes.[1] For example, a solution 5.88 g. (0.02 mole) of 5,6-dibromobenzofurazan oxide in 100 ml. of hot 95% ethanol was cooled rapidly in an ice bath to produce a finely divided suspension. A solution of 2.2 g. (0.032 mole) of hydroxylamine hydrochloride in 12 ml. of water was added followed by 25% aqueous potassium hydroxide with stirring and cooling until nitrogen evolution ceased. Steam distillation of the deep red alkaline solution gave 3.88 g. (69%) which was chromatographed in *n*-hexane on silica gel. Evaporation of the eluate and crystallization of the residue from *n*-hexane gave 5,6-dibromobenzofurazan as long colorless needles, m.p. 87–87.5°.

Anal. Calcd. for $C_6H_2Br_2N_2O$: C, 25.93; H, 0.73; N, 10.08. Found: C, 26.27; H, 1.04; N, 9.78.

4,5-Dibromobenzofurazan was obtained in 43% yield from IIa, forming colorless needles from 95% ethanol, m.p. 123–124°.

Anal. Calcd. for $C_6H_2Br_2N_2O$: C, 25.93; H, 0.73; N, 10.08. Found: C, 26.02; H, 0.95; N, 9.83.

4,6-Dibromobenzofurazan was obtained in 55% yield from IIb, forming long colorless needles from 95% ethanol, m.p. 71.5–72°.

Anal. Calcd. for $C_6H_2Br_2N_2O$: C, 25.93; H, 0.73; N, 10.08. Found: C, 26.23; H, 0.93; N, 9.98.

4,7-Dibromobenzofurazan was obtained in 69% yield from IIc, forming colorless needles from 95% ethanol, m.p. 112–112.5°, lit.[1] m.p. 113°.

Conversion of Tetrabromotetrahydrobenzofurazan Oxide (I) to Dibromobenzofurazan Oxide. A. With Pyridine.—A solution of 4.56 g. (0.01 mole) of I, m.p. 169–170°,[1] in 25 ml. of pyridine was allowed to stand at 25° for 2 hr. The suspension was poured into cold water and the resulting yellow precipitate was filtered, washed with water, and dried. The yield was 2.62 g. (89% based on conversion to dibromobenzofurazan oxide). Recrystallization twice from *n*-hexane and once from 95% ethanol gave 0.70 g. of yellow needles, m.p. 148–149°. This material was identical (mixture melting point and infrared spectrum) with 4,5-dibromobenzofurazan oxide obtained by the decomposition of IIIa as previously described.

The hexane filtrates were combined and evaporated to a small volume to yield 0.96 g., m.p. 70–89°. Recrystallization from aqueous dioxane and then from 95% ethanol gave 0.55 g. of yellow plates, m.p. 92.5–93°. This material was identical (mixture melting point and infrared spectrum) with 4,6-dibromobenzofurazan oxide obtained by the decomposition of IIIb, previously described.

B. With Potassium Acetate in Acetic Acid.—A mixture of 22.8 g. (0.05 mole) of I and 22 g. of potassium acetate in 200 ml. of glacial acetic acid was refluxed for 24 hr. The suspension was poured into water and the resulting solid was filtered, washed with water, and recrystallized twice from 95% ethanol and once from acetic acid. The yield of high-melting isomer, m.p. 148–149°, was 4.4 g.

The acetic acid filtrate was evaporated to a small volume giving 2.2 g., m.p. 77–80°, which after recrystallization from methanol weighed 1.4 g. Two recrystallizations from *n*-hexane gave an additional 0.17 g. of the high-melting isomer. The *n*-hexane filtrates were combined and evaporated to a small volume; the resulting solid was recrystallized from aqueous dioxane and then 95% ethanol. The yield of the low-melting isomer, m.p. 92.5–93°, was 0.59 g.

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Methyl 4-Deoxy-4-mercapto-D-ribofuranoside[1]

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Received May 19, 1964

This laboratory and others have been engaged in producing modified sugars wherein the ring oxygen is replaced by another atom such as sulfur, selenium, or nitrogen. Most work has dealt with the placement of sulfur in the sugar ring. Many of the thiosugars thus far produced are of biological interest, such as the ana-

(1) Journal Paper No. 2285 of the Purdue Agricultural Experiment Station, Lafayette, Ind. Presented in part at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April, 1964.