Anal. Calcd. for $C_{14}H_{10}O_4$: C, 69.42; H, 4.16. Found: C, 69.51; H, 4.32.

Attempted Dehydrogenation of 3-Hexyl-2,5-dihydrofuran.—3-Hexyl-2,5-dihydrofuran prepared as described above for 3-phenyl-2,5-dihydrofuran had physical properties agreeing with those reported by Yur'ev.[6] When 1.54 g. (0.01 mole) of the olefin was heated with sulfur no hydrogen sulfide evolution at 200–250° occurred. Slow decomposition took place above this temperature and no identifiable product could be isolated from the reaction mixture. Attempts to accomplish dehydrogenation using sulfur in boiling dimethylformamide resulted in recovery (by steam distillation) of 72% of starting olefin.

NEW ORLEANS, LOUISIANA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Bromonitro and Related Derivatives of Dibenzo-*p*-dioxin

BY HENRY GILMAN AND JOSEPH J. DIETRICH

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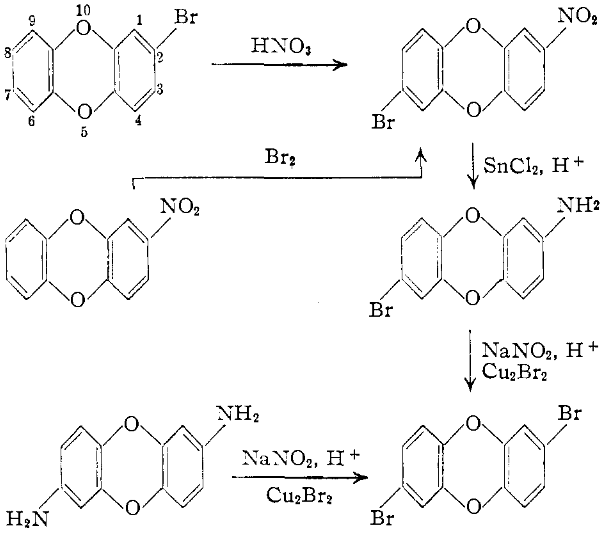
Several new derivatives of dibenzo-*p*-dioxin have been prepared while studying the directive influence of bromo and nitro substituents. Those chemically identified are 2-bromo-7-nitro-, 2-bromo-7-amino-, 2,7-diacetamido-, 2,7-dibromo- and 2,3,7,8-tetranitrodibenzo-*p*-dioxin. Infrared spectra were used to assign the structures of 2,3-dibromo-7-nitro- and 2-bromo-3,7-dinitrodibenzo-*p*-dioxin. Two compounds were designated as 2,8-dibromo-3,7-dinitro- and possibly 2,3-dibromo-7,8-dinitrodibenzo-*p*-dioxin since they are closely related to 2,3,7,8-tetrabromo- and 2,3,7,8-tetranitrodibenzo-*p*-dioxin.

In the course of studying the directive influence of various substituents on the dibenzo-*p*-dioxin nucleus, a number of interesting compounds was obtained. These have been characterized by a combination of chemical and physical methods.

The nitration of dibenzo-*p*-dioxin has been shown to proceed stepwise to yield 2-nitro-, 2,7- or 2,8-dinitro-, and finally 2,3,7-trinitrodibenzo-*p*-dioxin.[1] Bromination, in a similar manner, proceeds from the 2-bromo- to the 2,8-dibromodibenzo-*p*-dioxin in addition to a compound considered to be the 2,7-dibromo- and then to the 2,3,7,8-tetrabromodibenzo-*p*-dioxin.[2]

Nitration of 2-bromodibenzo-*p*-dioxin or bromination of 2-nitrodibenzo-*p*-dioxin resulted in the same product, the identity of which was established by reducing it to the amine and then forming the dibromo compound *via* a diazotization reaction. This dibromo compound proved to be the same as the dibromo compound obtained *via* the diazotization of 2,7-diaminodibenzo-*p*-dioxin, a known compound. Also helping to tie the above compounds together was the Beckmann rearrangement carried out on the dioxime of 2,7-diacetyldibenzo-*p*-dioxin. This reaction produced a diacetamido compound identical to that obtained by acetylating 2,7-diaminodibenzo-*p*-dioxin. A large discrepancy between the reported melting points of 2,7-dinitro-, 2,7-diaminodibenzo-*p*-dioxin[1] and the melting points, which were higher, obtained from the same compounds prepared in this Laboratory made the last sequence of reactions imperative.



A compound considered earlier to be the 2,7-dibromodibenzo-*p*-dioxin has been shown to be another isomer. This isomer may well be 2,3-dibromodibenzo-*p*-dioxin since its infrared spectrum, run in carbon disulfide, has a strong 1,2-disubstitution band at 13.3 μ, indicating that one ring was unsubstituted. When a Nujol mull was used, as in the previous paper,[2] the band at 13.3 μ was absent from the spectrum. Chemical evidence presented in the previously mentioned paper[2] is also consistent with the proposed structure.

2-Nitrodibenzo-*p*-dioxin may be brominated to yield a dibromonitrodibenzo-*p*-dioxin. Likewise, 2-bromodibenzo-*p*-dioxin may be dinitrated. Bromination[2] and nitration[1] studies fairly well limit the substituents to the 2,3,7-positions. Monobromination of 2-nitrodibenzo-*p*-dioxin and mononitration of 2-bromodibenzo-*p*-dioxin have been shown to yield the same compound. Therefore, only the position of the last group was in question. Working only with infrared data, the assignments of the two compounds in question are believed to be 2,3-dibromo-7-nitro- and 2-bromo-3,7-dinitrodibenzo-*p*-dioxin. Both compounds have a 1,2,4-trisubstitution band at 12.2 μ. This is consistent with the band found in the spectrum of 2-nitrodibenzo-*p*-dioxin at 12.2 μ but not with the band found in the spectrum of 2-bromodibenzo-*p*-dioxin at 12.4 μ. Therefore, one ring must contain the nitro group which was responsible for the band at 12.2 μ while the other ring contains the other two groups. Both assignments are theoretically sound when directive effects of the substituents already present are considered.

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[1] M. Tomita, *J. Pharm. Soc. Japan*, **55**, 1060 (1935) [*C. A.*, **31**, 6661 (1937)].

[2] H. Gilman and J. J. Dietrich, THIS JOURNAL, **79**, 1439 (1957).

Exhaustive nitration of dibenzo-*p*-dioxin or 2,7-dinitrodibenzo-*p*-dioxin produced a tetranitro derivative which has been designated 2,3,7,8 because the 2,3,7-trinitro derivative serves as an intermediate.[1] Using tetranitration and tetrabromination[2] of dibenzo-*p*-dioxin as analogies, it seems reasonable to assume that dinitration of 2,8-dibromodibenzo-*p*-dioxin would follow the same course. The derivative obtained in this manner has been, therefore, designated as the 2,8-dibromo-3,7-dinitrodibenzo-*p*-dioxin. Nitration of the dibromodibenzo-*p*-dioxin isomer considered to be 2,3-dibromodibenzo-*p*-dioxin produced a dibromodinitro compound, presumably 2,3-dibromo-7,8-dinitrodibenzo-*p*-dioxin. This material has no 1.2-disubstitution band in its spectrum.

Bromination of 2-aminodibenzo-*p*-dioxin in carbon tetrachloride yielded an amino-bromo compound which was not characterized.

Experimental[3]

2-Bromo-7-nitrodibenzo-*p*-dioxin. Run I.—A mixture of 2 g. (0.0087 mole) of 2-nitrodibenzo-*p*-dioxin, 3.6 g. (0.029 mole) of potassium bromide, 1 g. (0.0058 mole) of potassium bromate, 5 ml. of water and 50 ml. of glacial acetic acid was refluxed for 1.5 hr. The reaction mixture was then diluted with a sodium bisulfite solution and filtered. Three recrystallizations of the crude material from glacial acetic acid yielded 0.6 g. (23%) of yellow needles, m.p. 215–217°.

Anal. Calcd. for $C_{12}H_6O_4NBr$: N, 4.60. Found: N, 4.41, 4.32.

Run II.—A solution of 1.5 g. (0.005 mole) of 2-bromodibenzo-*p*-dioxin, 2 ml. of concentrated nitric acid and 20 ml. of glacial acetic acid was heated to 50–60° for 10 min. The solution turned green-yellow in color. After cooling, the reaction mixture was diluted with water and filtered. Four recrystallizations of the material from glacial acetic acid resulted in the isolation of less than 0.1 g. of yellow needles, m.p. 214–216°. A mixture melting point of this material with that obtained in run I showed no depression.

When the same reaction was run at 18°, there was a near quantitative recovery of starting material.

2-Amino-7-bromodibenzo-*p*-dioxin.—A solution of 12 g. (0.041 mole) of anhydrous tin(II) chloride in 25 ml. of concentrated hydrochloric acid was added slowly to a hot solution of 4.3 g. (0.014 mole) of 2-bromo-7-nitrodibenzo-*p*-dioxin in 25 ml. of glacial acetic acid. The resulting solution was heated for 10 min. at which time the yellow color had disappeared. The mixture, now containing a white precipitate, was made strongly basic with aqueous potassium hydroxide and then filtered. Recrystallization of the crude material from ethanol–water (Norit A) formed 3 g. of product melting 150–170°. One gram of this material was recrystallized three times from benzene to yield 0.3 g. (23%) of white needles melting 180–183°. An infrared spectrum of this compound showed that total reduction had taken place since the band characteristic of the nitro group was absent from the spectrum.

Anal. Calcd. for $C_{12}H_8O_2NBr$: N, 5.04. Found: N, 4.90, 4.96.

2,7-Dibromodibenzo-*p*-dioxin. Run I.—A solution of 2 g. (0.007 mole) of 2-amino-7-bromodibenzo-*p*-dioxin in 25 ml. of glacial acetic acid cooled to 18° was diazotized with 8 ml. of nitrosylsulfuric acid according to the procedure of Saunders.[4] The resulting mixture was stirred for 10 min. and then added at 5° to a hydrobromic acid solution of freshly prepared copper(I) bromide.[5] The mixture was heated to 80°, diluted with water and filtered. After drying under a heat lamp, the crude material was dissolved in benzene and chromatographed on alumina. Evaporation of the excess eluate followed by two recrystallizations from benzene produced 0.6 g. (25%) of light yellow plates, m.p. 197–198°.

Anal. Calcd. for $C_{12}H_6O_2Br_2$: Br, 46.75. Found: Br, 46.31, 46.54.

Run II.—A solution of 4.5 g. (0.021 mole) of 2,7-diaminodibenzo-*p*-dioxin in 50 ml. of glacial acetic acid was diazotized as in the preceding experiment. The mixture was stirred for 10 min. after addition and then added to a solution of copper(I) bromide[5] at 5°. A brown complex formed which was destroyed by heating the mixture to 80°. Dilution with water followed by filtration produced crude material which was dissolved in benzene and chromatographed on alumina. Evaporation of the eluate followed by four recrystallizations from glacial acetic acid yielded 1.2 g. (17%) of product, m.p. 195–197°. A mixture melting point with material from run I showed no depression. Comparison of their infrared spectra served as an additional check.

2,7-Diacetamidodibenzo-*p*-dioxin. Run I.—A Beckmann rearrangement was run on 1.7 g. (0.006 mole) of 2,7-diacetyldibenzo-*p*-dioxin dioxime using 4.2 g. (0.02 mole) of phosphorus chloride in 150 ml. of sodium-dried benzene. During the slow addition of phosphorus chloride, a yellow color developed. After addition, the mixture was stirred for 18 hr. at room temperature, hydrolyzed with dilute sodium carbonate solution and a yellow solid filtered from the benzene layer. Two recrystallizations of this solid from acetic acid–water produced 0.8 g. (47%) of tan colored needles, m.p. 354–356° dec.

Anal. Calcd. for $C_{16}H_{14}O_4N_2$: N, 9.40. Found: N, 8.88, 8.84.

Run II.—A mixture of 1 g. (0.005 mole) of 2,7-diaminodibenzo-*p*-dioxin and 30 ml. of benzene was refluxed while 2 g. (0.02 mole) of acetic anhydride was added slowly. Refluxing was continued for 0.5 hr. at which time the mixture was cooled and filtered. The crude material, filtered from the benzene layer, was recrystallized twice from glacial acetic acid to yield 1 g. (66%) of tan needles, m.p. 356–357° dec. A mixture melting point with the material from run I showed no depression.

2,3-Dibromo-7-nitrodibenzo-*p*-dioxin.—A solution of 2.7 g. (0.011 mole) of 2-nitrodibenzo-*p*-dioxin, 8 g. (0.05 mole) of bromine and 50 ml. of glacial acetic acid was stirred and refluxed for 5.5 hr. The reaction mixture was diluted with a sodium bisulfite solution and filtered. Extraction of the crude material with ethanol left a residue which was recrystallized three times from glacial acetic acid to yield a small quantity of yellow crystalline material melting 217–220°. This range could not be altered by recrystallizations from other solvents. From a previous experiment (see 2-bromo-7-nitrodibenzo-*p*-dioxin, run I), it is assumed that some 2-bromo-7-nitrodibenzo-*p*-dioxin is present. It was impossible to check for this impurity through the use of infrared spectra.

Anal. Calcd. for $C_{12}H_5O_4NBr_2$: Br, 41.45. Found: Br, 40.45, 40.69.

2-Bromo-3,7-dinitrodibenzo-*p*-dioxin.—To a solution of 50 ml. of concentrated nitric acid at ice-bath temperature was added slowly 1.3 g. (0.005 mole) of 2-bromodibenzo-*p*-dioxin. The now yellow mixture was allowed to warm to room temperature, stirred for 10 hr., diluted with water and filtered. Three recrystallizations of the crude material from ethanol produced 0.5 g. (28%) of yellow needles, m.p. 190–192°.

Anal. Calcd. for $C_{12}H_5O_6N_2Br$: N, 8.00. Found: N, 8.07, 8.11.

2,3,7,8-Tetranitrodibenzo-*p*-dioxin. Run I.—A solution consisting of 150 ml. of concentrated nitric acid and 100 ml. of concentrated sulfuric acid was cooled to ice-bath temperature while 9.2 g. (0.05 mole) of dibenzo-*p*-dioxin was added in small portions. After addition, the temperature was slowly raised to 90° over a period of 1 hr. and then allowed to cool. Dilution with water, filtration, one recrystallization of the crude material from pyridine and two recrystallizations from acetic anhydride produced 3.1 g. (17%) of red-brown needles, m.p. 334–335° dec.

Anal. Calcd. for $C_{12}H_4O_{10}N_4$: N, 15.38. Found: N, 14.79, 14.66.

Run II.—A mixture of 1.7 g. (0.006 mole) of 2,7-dinitrodibenzo-*p*-dioxin, 50 ml. of concentrated nitric acid and 50 ml. of fuming nitric acid was warmed slowly to 60° over a period

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(3) All melting points are uncorrected.

(4) K. H. Saunders, "The Aromatic Diazo Compounds," Edward Arnold and Co., London, 1949, p. 13.

(5) W. C. Fernelius, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 3.

of 2 hr. Dilution of the reaction mixture with water followed by filtration produced 1.9 g. of crude material which was recrystallized once from pyridine and three times from acetic anhydride to yield 0.4 g. (18%) of red-brown needles melting 330–333° dec. A mixture melting point with material from run I showed no depression.

2,8-Dibromo-3,7-dinitrodibenzo-*p*-dioxin.—To a stirred solution of 50 ml. of concentrated nitric acid and 30 ml. of concentrated sulfuric acid was added slowly 1.5 g. (0.0044 mole) of 2,8-dibromodibenzo-*p*-dioxin at room temperature. Stirring was continued for 20 min. at room temperature, the mixture warmed to 60° and then allowed to cool. Dilution of the reaction mixture, then filtration, produced 1.5 g. of crude material. Four recrystallizations from glacial acetic acid yielded 0.5 g. (26%) of yellow needles, m.p. 276–278°.

Anal. Calcd. for $C_{12}H_4O_6N_2Br_2$: N, 6.48. Found: N, 6.51, 6.38.

2,3-Dibromo-7,8-dinitrodibenzo-*p*-dioxin.—A solution of 0.5 g. of dibromo compound and 10 ml. of glacial acetic acid was cooled to ice-bath temperature. Then 5 ml. of concentrated nitric acid was added. The temperature was slowly raised to reflux and held there for 0.5 hr. Dilution of the reaction mixture and then three recrystallizations of the crude material from benzene–petroleum ether (b.p. 60–70°) resulted in the isolation of 0.3 g. of yellow plates melting at 267–270°.

Anal. Calcd. for $C_{12}H_4O_6N_2Br_2$: N, 6.48. Found: N, 6.35, 6.40.

2-Amino-X-bromodibenzo-*p*-dioxin.—A solution of 2 g. (0.01 mole) of 2-aminodibenzo-*p*-dioxin, 3.6 g. (0.02 mole) of bromine and 100 ml. of carbon tetrachloride was stirred for 2.5 hr. at room temperature. The now green solution was washed with aqueous sodium bisulfite and then dilute potassium hydroxide. Evaporation of the carbon tetrachloride layer and then two recrystallizations of the residue from ethanol–water resulted in the isolation of 0.8 g. (28%) of fine, pink needles, m.p. 152–154°. The infrared spectrum has a sharp band at 13.3 μ, indicating that both groups are in one ring. However, there is no simple way of determining the position of the bromine atom.

Anal. Calcd. for $C_{12}H_8O_2NBr$: Br, 28.77. Found: Br, 29.33, 29.37.

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AMES, IOWA

[CONTRIBUTION FROM THE NAVAL STORES STATION, U. S. DEPARTMENT OF AGRICULTURE[1]]

A Preparation and Some of the Properties of *trans*-6,14-Dihydrolevopimaric Acid-6,14-*endo*-α,β-succinic Acid

BY NOAH J. HALBROOK AND RAY V. LAWRENCE

RECEIVED AUGUST 29, 1957

Rosin and the abietic-type acids of rosin were found to undergo a normal Diels–Alder type condensation with fumaric acid to yield tricarboxylic acids. A practical procedure is presented for separating the major reaction product, one of the isomers of *trans*-6,14-dihydrolevopimaric-acid-6,14-*endo*-α,β-succinic acid, as a crystalline hemihydrate. By means of partition chromatography a non-crystalline tricarboxylic acid was obtained as a minor product from the residual resin. Infrared spectra and neutralization equivalents indicate the crystalline and non-crystalline acids to be geometric isomers. The crystalline isomer was converted to maleopimaric acid when heated at 280°. Isodextropimaric acid, one of the pimaric-type acids of rosin, did not react with fumaric acid under conditions commonly employed.

The patent literature contains many references to the reaction of rosin with fumaric acid. The modified rosin has commercial value in the formulation of materials such as coating compositions and printing inks. Information is not available on the chemical composition of the modification. It was therefore of interest to examine the products resulting from the treatment of the individual resin acids and rosin with fumaric acid and to characterize the major products of this reaction.

Levopimaric acid which is present in gum oleoresin condenses at room temperature with maleic anhydride to form the Diels–Alder addition compound,[2] maleopimaric acid. During distillation of oleoresin, the levopimaric acid present isomerizes to other resin acids, the end products of the thermal isomerization being abietic, neoabietic and palustric acid.[3] All of these acids react with maleic anhydride under vigorous reaction conditions to form maleopimaric acid.[4] To account for a normal Diels–Alder reaction of the abietic-type acids it has been assumed that levopimaric acid is in equilibrium with abietic acid under conditions[5] required for the reaction. Maleopimaric acid in alkali and under high temperature and pressure has been reported to isomerize[6] to fumaropimaric acid[7] (I), the expected product if the less reactive dienophile, fumaric acid, forms the normal Diels–Alder reaction product with levopimaric acid. However, the products obtained from direct combination of fumaric acid and rosin have not been investigated.

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(1) One of the laboratories of the Southern Utilization Research & Development Division, Agricultural Research Service, U. S. Department of Agriculture. Article not copyrighted.

(2) (a) R. G. R. Bacon and L. Ruzicka, *Chemistry & Industry*, 546 (1936); (b) H. Wienhaus and W. Sandermann, *Ber.*, **69**, 2202 (1936).

(3) (a) V. M. Loeblich, D. E. Baldwin, R. T. O'Connor and R. V. Lawrence, THIS JOURNAL, **77**, 6311 (1955); (b) J. Köhler, *J. prakt. Chem.*, **85**, 534 (1912); (c) L. Ruzicka, F. Balas and F. Vilim, *Helv. Chim. Acta*, **7**, 458 (1924).

(4) (a) V. M. Loeblich, D. E. Baldwin and R. V. Lawrence, THIS JOURNAL, **77**, 2823 (1955); (b) B. Arbuzov, *J. Gen. Chem., U.S.S.R.*, **2**, 806 (1932) (*C. A.*, **27**, 2688 (1933)).

(5) L. F. Fieser and W. P. Campbell, THIS JOURNAL, **60**, 159 (1938).

(6) G. C. Harris (to Hercules Powder Co.), U. S. Patent 2,517,563, August 8, 1950.

(7) Fumaropimaric acid is the trivial name for *trans*-6,14-dihydrolevopimaric-acid-6,14-*endo*-α,β-succinic acid. The conventional name used here is analogous to that previously used in naming anthracene adducts. See W. E. Bachmann and L. B. Scott, THIS JOURNAL, **70**, 1458 (1948). The prefix *trans* refers to the configuration about the central C–C bond of the succinic acid grouping. The crystalline fumaropimaric acid isomer, isolated here as the major product of the reaction discussed, will be referred to simply as fumaropimaric acid. When the non-crystalline isomer of fumaropimaric acid is discussed it will be so designated.