solution); 5% at 100° in the presence of an aqueous solution containing 75% of zinc chloride. Glacial acetic, mono- and dichloro acetic acids caused no isomerization at 100°.

Isomerization of *trans*-2-Butene by Phosphoric Acid.—Pure *trans*-2-butene (450 ml. per hour) on passage through 36 g. of 100% orthophosphoric acid at 100° (Fig. 1) underwent partial isomerization to a mixture containing 6.6% 1-butene, 6.0% *cis*- and 87.4% *trans*-2-butene.

Summary

1. Isomerization of 1- into 2-butene was slight in the presence of phosphoric acid at room temperature and increased with rising temperature. A similar increase in isomerization of 1- into 2-butene with temperature rise was observed under pressure in the presence of diatomaceous earth impregnated with phosphoric acid. At 249° isomerization was complete under 7.8 atmospheres pressure.

2. Pure *trans*-2-butene underwent partial isomerization into 1-butene (6.6%) and *cis*-2-butene (6.0%) during passage through 100% orthophosphoric acid at 100°.

3. 1-Butene isomerized partially into the 2-isomer in the presence of perchloric acid and aqueous solutions of zinc chloride and benzene sulfonic acid.

RIVERSIDE, ILLINOIS RECEIVED SEPTEMBER 10, 1934

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA. NO. 147]

Di-(*p*-bromophenyl)-furans and 1,4-Diketones

BY ROBERT E. LUTZ AND W. M. EISNER

This paper deals with the preparation of some new compounds of this series and some further studies of typical reactions.[1]

The nitric–acetic acid oxidation[1i] of 2,5-di-(*p*-bromophenyl)-3,4-dichloro and dibromofurans (I) gives in good yields the corresponding *cis* di-(bromobenzoyl)-dihalogenoethylenes III. The configurations are based on the fact that these compounds are the labile forms and are converted by the action of sunlight on a chloroform solution containing iodine into the stable and therefore *trans* isomers.[1d] The synthesis of the *trans* dibromo isomer IV from dibromofumaryl chloride II by the Friedel–Crafts reaction confirms these configurations (see Diagram 1). All four of these dihalogenoethylenes are reduced with ease by means of zinc and glacial acetic acid to di-(bromobenzoyl)-ethane V (known[2]).

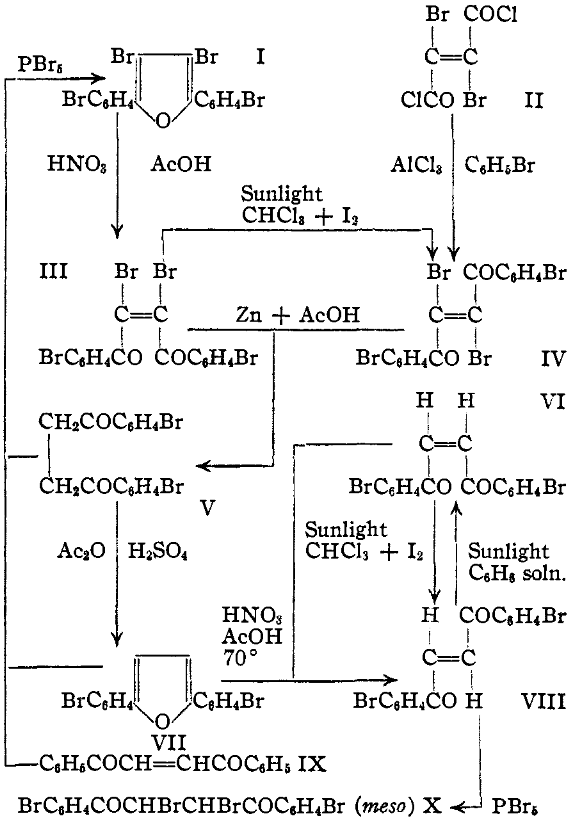

DIAGRAM 1.

2,5-Di-(bromophenyl)-furan VII, prepared by the action of acetic anhydride and sulfuric acid on di-(bromobenzoyl)-ethane V, is easily oxidized by the nitric–acetic acid method, giving however the *trans* di-(bromobenzoyl)-ethylene VIII. The *cis* isomer VI[3] is undoubtedly first formed in the oxidation; it may be prepared by exposing a benzene solution of the *trans* isomer to the sunlight, and is very easily rearranged back into the *trans* isomer, either by the nitric–glacial acetic

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[1] *Cf.* (a) Conant and Lutz, THIS JOURNAL, **47**, 881 (1925); Lutz, *ibid.*, (b) **48**, 2905 (1926); (c) **51**, 3008 (1929); **52**, (d) 3405, (e) 3423 (1930); Lutz and Taylor, *ibid.*, **55**, (f) 1168, (g) 1585, (h) 1593 (1933); Lutz and Wilder, *ibid.*, **56** (i) 979, (j) 2145 (1934).

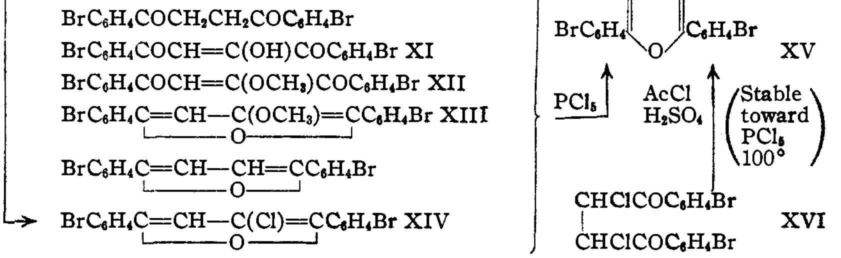
[2] Hale and Thorpe, *ibid.*, **35**, 272 (1913).

[3] We are indebted to Mr. P. A. Whitaker for the isolation of this compound.

acid reagent under the conditions involved in the oxidation of the furan, or by means of iodine in chloroform solution with the aid of sunlight.

Phosphorus pentabromide reacts with di-(bromobenzoyl)-ethane V and with di-(bromophenyl)-furan VII to give di-(bromophenyl)-dibromofuran I (known[4]). *Trans* di-(bromobenzoyl)-ethylene VIII under these conditions adds bromine, giving the stable *meso* di-(bromobenzoyl)-dibromoethane X in contrast with dibenzoylethylene (IX) which gives di-(bromophenyl)-dibromofuran. Neither the *dl* nor the *meso* di-(bromobenzoyl)-dibromoethanes are acted upon by this reagent. The mechanism of the formation of furans from the unsaturated 1,4-diketones very probably involves conjugate addition.[1i] It would appear that the reactivity of the conjugated system toward phosphorus pentabromide is affected more by the para bromines than is the reactivity of the double bond toward addition of bromine (which is ever present through dissociation of the reagent).

The action of phosphorus pentachloride at 100–150° on various of the saturated and unsaturated 1,4-diketones of this series, and on some of the furans, gives di-(*p*-bromophenyl)-dichlorofuran XV. These reactions parallel those of the diphenyl analogs[1j] and are summarized in Diagram 2. It is noteworthy that the methoxyl group as well as the beta hydrogen of di-(bromophenyl)-methoxyfuran XIII are replaceable with chlorine to give the dichlorofuran XV. This reaction is of some importance in that it confirms the structure of the methoxy furan XIII.[1c] The corresponding diphenylmethoxyfuran also reacts easily with phosphorus pentachloride but gives non-crystalline products.



(*a*) AcCl + H_2SO_4 Diagram 2.

It is noteworthy that in the phenylated furan series a methoxyl or acetoxyl group is replaceable easily by halogen. These reactions are not commonly reported among benzene analogs. Anisole, for example, is halogenated by phosphorus pentachloride without affecting the methoxyl group,[5] and *p*-cresyl benzoate with phosphorus pentabromide undergoes hydrolysis and bromination in the ortho positions, the phenolic hydroxyl group remaining intact.[6]

Incidental to this research, *trans* β-(*p*-bromobenzoyl)-dibromoacrylic methyl ester XIX was made by the Friedel–Crafts reaction on dibromofumaric monomethyl ester monochloride XX. The latter compound, used previously in an impure state,[1d] was made through partial hydrolysis of dibromofumaric dimethyl ester XVII, and subsequent action of phosphorus pentachloride on the resulting monomethyl acid ester XVIII (Diagram 3). In attempted hydrolysis of XIX to the corresponding acid, fission of the molecule occurred, giving *p*-bromobenzoic acid and proving the position of the bromine atom in the phenyl nucleus.

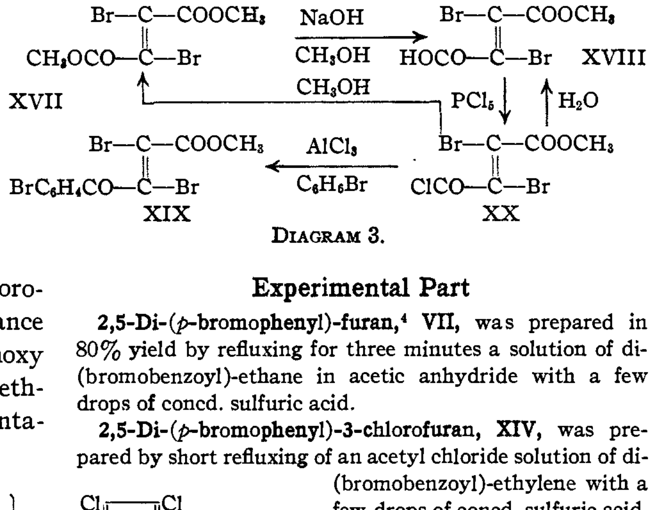


Diagram 3.

Experimental Part

2,5-Di-(*p*-bromophenyl)-furan,[4] VII, was prepared in 80% yield by refluxing for three minutes a solution of di-(bromobenzoyl)-ethane in acetic anhydride with a few drops of concd. sulfuric acid.

2,5-Di-(*p*-bromophenyl)-3-chlorofuran, XIV, was prepared by short refluxing of an acetyl chloride solution of di-(bromobenzoyl)-ethylene with a few drops of concd. sulfuric acid. It crystallized as fine needles from benzene; m. p. 120°; yield 60%.

Anal. Calcd. for $C_{16}H_9OBr_2Cl$: C, 46.6; H, 2.2. Found: C, 46.9; H, 2.15.

2,5-Di-(*p*-bromophenyl)-3,4-dichlorofuran, XV, was prepared by heating the following with five parts of phosphorus pentachloride at temperatures of 100–150°; VII (yield 85–95%), V (80%), VIII (60%), XII (80%), XI (60%), XIV (90%), and XIII. *dl* and *meso*

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[4] Thiele and Rosner, *Ann.*, **306**, 41 (1899); Perkin and Schloesser, *J. Chem. Soc.*, **57**, 947 (1890).

[5] Henry, *Ber.*, **2**, 711 (1869); Hayashi, *J. prakt. Chem.*, **123**, 306 (1929).

[6] Raiford and Milbery, This Journal, **56**, 2727 (1934).

di-(bromobenzoyl)-dichloroethanes failed to react under these conditions. The *dl* isomer was converted in 80% yield into the furan by refluxing for ten minutes an acetic anhydride solution containing a few drops of concd. sulfuric acid. The various reaction mixtures were decomposed in ice and water and the products crystallized from glacial acetic acid. The pure product melts at 166°.

Anal. Calcd. for $C_{16}H_8OCl_2Br_2$: C, 43.0; H, 1.8. Found: C, 42.8; H, 1.7.

2,5-Di-(*p*-bromophenyl)-3,4-dibromofuran,[4] **I,** was prepared by heating VII or V with five parts of phosphorus pentabromide at 90°, decomposing the mixtures with ice, and recrystallizing the products from glacial acetic acid; yields 90–95% and 75%, respectively.

Trans **1,2-di-(*p*-bromobenzoyl)-ethylene,**[1b] **VIII,** was prepared by the nitric–glacial acetic acid oxidation of 2,5-di-(bromophenyl)-furan in the usual way[1i] at 70°. When the reaction was carried out at refluxing temperature *p*-bromobenzoic acid was obtained. When VIII was treated with five parts of phosphorus pentabromide at 90–100°, an 89% yield of *meso* di-(bromobenzoyl)-dibromoethane was obtained. The latter compound is not affected by boiling acetic anhydride and concd. sulfuric acid.

Cis **1,2-di-(*p*-bromobenzoyl)-ethylene,**[3] **VI,** was prepared by exposing a benzene solution of the *trans* isomer to strong sunlight for one day, evaporating the solvent under reduced pressure, and recrystallizing the residue from ethanol. An insoluble residue and the first crop of crystals obtained on cooling to 40–50° were unchanged material which is very difficultly soluble in ethanol. Upon cooling the filtrate and then adding water, two successive crops of nearly pure *cis* isomer were obtained and recrystallized from ethanol as needles of m. p. 124.5–125° (corr.).

Anal. Calcd. for $C_{16}H_{10}O_2Br_2$: Br, 40.6. Found: Br, 40.7. Mol. wt. (Rast) calcd., 394. Found: 389, 398.

The *cis* isomer was transformed completely into the *trans* isomer when (a) exposed for fifteen minutes to sunlight in a chloroform solution containing iodine, and (b) heated for a few minutes at 70° in glacial acetic acid containing a little concd. nitric acid (the *trans* isomer separating as leaflet crystals).

Cis **1,2-di-(*p*-bromobenzoyl)-1,2-dibromoethylene, III,** was prepared by the nitric–glacial acetic acid oxidation[1i] of I at 70°; yield 80%. It crystallized as needles from ligroin–benzene mixtures; m. p. 112.5°.

Anal. Calcd. for $C_{16}H_8O_2Br_4$: C, 34.8; H, 1.4. Found: C, 35.2; H, 1.8.

Reduction with zinc and glacial acetic acid (refluxing for several minutes) gave V in 80% yield. Conversion into the *trans* isomer was brought about by the action of sunlight on a chloroform solution containing iodine (yield 50%).

Trans **1,2-di-(*p*-bromobenzoyl)-1,2-dibromoethylene, IV,** was prepared by adding 5 g. of dibromofumaryl chloride dropwise (mechanical stirring) to a mixture of 30 cc. of bromobenzene and 10 g. of finely pulverized aluminum chloride with carbon disulfide as solvent, refluxing for thirty minutes, and hydrolyzing in ice and hydrochloric acid. The insoluble product was filtered off and recrystallized from bromobenzene; m. p. 235.5°; yield, 60%.

Anal. Calcd. for $C_{16}H_8O_2Br_2$: C, 34.8; H, 1.4. Found: C, 35.2; H, 1.4.

It is noteworthy that in this reaction, **and also in** the analogous one with fumaryl chloride,[1b] **two molecules of** bromobenzene react in the Friedel–Crafts reaction, but in the case of mesaconyl chloride, only one molecule of bromobenzene reacts, although further reaction can be accomplished on β-bromobenzoylcrotonic and methylacrylic acid chlorides using benzene instead.[1b]

Reduction with zinc and glacial acetic acid in the usual way gave V.

Cis **1,2-di-(*p*-bromobenzoyl)-dichloroethylene, $BrC_6H_4COCCl{=}CClCOC_6H_4Br$,** was prepared by the nitric–glacial acetic acid oxidation of XV at 70°; yield 70%. It crystallized as long needles from glacial acetic acid; m. p. 111°. Oxidation at refluxing temperature gave *p*-bromobenzoic acid.

Anal. Calcd. for $C_{16}H_8O_2Cl_2Br_2$: C, 41.5; H, 1.7. Found: C, 41.6; H, 1.5.

Reduction with zinc and glacial acetic acid gave V.

Trans **1,2-di-(*p*-bromobenzoyl)-dichloroethylene, $BrC_6H_4COCCl{=}CClCOC_6H_4Br$,** was prepared by the action of sunlight on the *cis* isomer in chloroform solution containing iodine. It crystallized from butanone as rhombohedra of m. p. 206° (corr.).

Anal. Calcd. for $C_{16}H_8O_2Cl_2Br_2$: ClBr, 49.82. Found: ClBr, 49.91.

Dibromofumaric Monomethyl Acid Ester, XVIII.—A solution of 15 g. of dibromofumaric dimethyl ester XVII and 2.8 g. of potassium hydroxide in 100 cc. of methanol was allowed to stand for seventy-two hours. The solution was concentrated by evaporation under reduced pressure, diluted with water, and extracted with ether to remove unchanged material. The aqueous layer was evaporated nearly to dryness under reduced pressure and the residue acidulated with hydrochloric acid, the monomethyl ester separating as an oil which was extracted with ether. The oil solidified on drying in a vacuum desiccator for a few days. It crystallized as thin scales from ligroin. It is very hygroscopic and liquefies in a short time upon exposure to moist air; m. p. 75°; yield 50%.

Anal. Calcd. for $C_5H_4O_4Br_2$: C, 20.8; H, 1.4. Found: C, 20.9; H, 1.55.

Hydrolysis of 0.5 g. with methanolic sodium hydroxide (twenty hours at 25°) gave 0.42 g. of dibromofumaric acid.

Dibromofumaric monomethyl ester monochloride, XX, was prepared by the action of phosphorus pentachloride on the above acid ester, being separated from the phosphorus oxychloride by fractional distillation under reduced pressure using a 15-cm. Vigreux column; b. p. 107–108° at 12 mm.

Anal. Calcd. for $C_5H_3O_3Br_2Cl$: C, 19.6; H, 1.0. Found: C, 19.7; H, 1.1.

Alcoholysis with methanol gave dibromofumaric dimethyl ester.

Heating with aluminum chloride at 100° gives dibromofumaric acid in a 20% yield.

The Friedel–Crafts reaction with benzene gave *trans* β-benzoyl-dibromoacrylic methyl ester in 92% yield. Hydrolysis of this product with an excess of aqueous sodium hydroxide (boiled for thirty minutes) gave an 80% yield of benzoic acid.

***Trans* β-(*p*-Bromobenzoyl)-dibromoacrylic Methyl Ester, XIX.**—Dibromofumaric monomethyl ester monochloride (4 g.) was added slowly with mechanical stirring to a mixture of carbon disulfide, 10 cc. of bromobenzene, and 5 g. of aluminum chloride. The mixture was stirred for one hour and heated for fifteen minutes, and then decomposed in ice and hydrochloric acid. The carbon disulfide solution was evaporated and the residue crystallized from ligroin; m. p. 102°; yield 66%.

Anal. Calcd. for $C_{11}H_7O_3Br_3$: C, 30.9; H, 1.68. Found: C, 30.9; H, 1.54.

The above preparation goes equally well using the crude acid chloride–phosphorus oxychloride mixture.

Hydrolysis of the ester using 80% ethanolic sodium hydroxide (standing at room temperature for two days) gave a nearly theoretical yield of *p*-bromobenzoic acid.

Summary

The nitric–glacial acetic acid oxidation of the di-(*p*-bromophenyl)-dihalogenofurans gives *cis* unsaturated 1,4-diketones, which may be rearranged into the stable *trans* isomers. The oxidation of di-(*p*-bromophenyl)-furan is described.

The di-(*p*-bromophenyl)-dihalogenofurans are formed by the action of phosphorus pentahalides on saturated and unsaturated 1,4-diketones and on the di-(*p*-bromophenyl)-furans.

Dibromofumaric monomethyl acid ester and its acid chloride are described.

UNIVERSITY, VIRGINIA RECEIVED SEPTEMBER 10, 1934

[CONTRIBUTION FROM THE NEW JERSEY AGRICULTURAL EXPERIMENT STATION]

Decomposition of Polyuronides by Fungi and Bacteria. II. Decomposition of Alginic Acid by Bacteria and Formation of the Enzyme Alginase[1]

BY SELMAN A. WAKSMAN AND MELVIN C. ALLEN

Alginic acid or algin, one of the carbohydrate constituents of marine algae, has attracted for many years the attention of chemists because of its abundance in nature and its specific chemical structure.[2] Kylin,[3] distinguished between algin and fucin, the first being soluble in hot water and the second only in dilute sodium carbonate solution; algin was believed to be the calcium salt of alginic acid and its solubility in hot water was explained by the substitution of an alkali base for the calcium. On hydrolysis with mineral acids, alginic acid was found to give reducing substances, which were at first thought to be pentoses; however, it was shown later that the furfural is produced not from a pentose group, but from an acidic nucleus, since, on boiling with hydrochloric acid, the algin or alginic acid preparations lost 20% of their weight as carbon dioxide. The constituent uronic acid was believed[4,5] to be glucuronic, but, more recently, it was found[6,7] to be *d*-mannuronic acid. According to Schmidt,[5] the polyuronic acid of *Fucus serratus* consists of two forms, *a*, highly resistant to chemical reagents, and *b*, readily hydrolyzed by mineral acids.

Very little is known concerning the fate of this polyuronide in the process of decomposition of marine algae in the sea and in other natural substrates; the fact that it makes up nearly 20 to 30% of the total organic matter of many of the algae would make a study of its decomposition under natural conditions of considerable interest. It has been definitely established[8,9] that the polymer of galacturonic acid, namely, pectic acid of fruits and vegetables, is readily decomposed by a great variety of microörganisms, especially fungi; these produce an enzyme which hydrolyzes the polyuronide into simpler units; the latter are readily oxidized further by the organisms in the process of their metabolism. It remained to be determined whether the process of decomposition of the polymer of mannuronic acid is similar in nature.

Experimental

As a source of alginic acid, freshly collected *Fucus vesiculosus* was used. The material was treated in the cold with 0.5% hydrochloric acid, to remove the bases, washed with water and extracted with approximately 0.5% solution of ammonia; the extract was precipitated with hydrochloric acid, giving a crude algin precipitate, which was washed with water, alcohol and ether, and dried. By the use of the chlorine dioxide reagent of Schmidt,[5] a fairly pure alginic acid was obtained, as shown by the presence of only a small amount of ash and nitrogen;

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(1) Journal Series paper of the New Jersey Agricultural Experiment Station, Department of Soil Microbiology.

(2) E. C. C. Stanford, *Chem. News*, **47**, 254, 267 (1883).

(3) H. Kylin, *Z. physiol. Chem.*, **83**, 171 (1913); **94**, 337 (1915).

(4) Atsuki and Tomada, *J. Soc. Chem. Ind. Japan*, **29**, 509 (1926).

(5) E. Schmidt and F. Vocke, *Ber.*, **59**, 1585 (1926).

(6) W. L. Nelson and L. H. Cretcher, THIS JOURNAL, **51**, 1914 (1929); **52**, 2130 (1930).

(7) J. M. Bird and P. Haas, *Biochem. J.*, **25**, 403 (1931).

(8) F. Ehrlich, *Biochem. Z.*, **250**, 525 (1932); **251**, 204 (1932).

(9) S. A. Waksman and M. C. Allen, THIS JOURNAL, **55**, 3408 (1933).