in complete qualitative agreement with experiment; agreement is obtained, however, by the consideration of the effect of polarization of the molecule by the attacking group. Because of the presence of several adjustable parameters, this treatment cannot be considered as a pure quantum mechanical theory of directed substitution in aromatic molecules. However, the various effects which we have considered are certainly real, and there is no reason to doubt that they act in the directions calculated, and are of the general order of magnitude assumed; the parameters introduced are not completely arbitrary in value, because they are related to definite and fairly well understood atomic and molecular quantities. Furthermore, in the cases in which only one effect is important, as in pyridine, or in which all effects act in the same direction, as in nitrobenzene, the calculations lead to completely unambiguous conclusions, which are dependent to only a small degree upon the particular parameter values chosen. We accordingly feel that the degree of success realized in these quantitative considerations provides strong support for the underlying ideas as to the nature of the effects involved.

Summary

Using the method of molecular orbitals, a quantitative discussion of the charge distribution in aromatic molecules undergoing substitution reactions is carried out, taking into consideration the inductive effect, the resonance effect, and the polarizing effect of the attacking group. It is shown that, with reasonable values for the parameters involved, the calculated charge distributions for pyridine, toluene, phenyltrimethylammonium ion, nitrobenzene, benzoic acid, benzaldehyde, acetophenone, benzonitrile, furan, thiophene, pyrrole, aniline, phenol, naphthalene, and the halogen benzenes are in qualitative agreement with the experimental results regarding position and rate of substitution, the auxiliary hypothesis being made that the rate of substitution of the group R′ for hydrogen on the *i*th carbon atom increases with increase in the negative charge of the *i*th carbon atom when the group R′ is in position to react.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Dibenzofuran. VII. Derivatives of Tetrahydrodibenzofuran

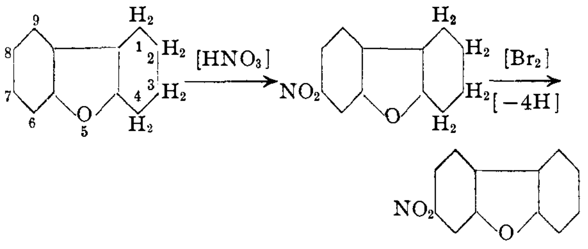
BY HENRY GILMAN, E. W. SMITH AND L. C. CHENEY

Introduction

The presence of a reduced dibenzofuran nucleus in morphine suggested an examination of nuclearly substituted reduced dibenzofurans. From the results of the present study on 1,2,3,4-tetrahydrodibenzofuran it appears (1) that the orientation of the parent dibenzofuran cycle is essentially unlike that of 1,2,3,4-tetrahydrodibenzofuran; (2) that the position assigned to the nitro group in nitro-1,2,3,4-tetrahydrodibenzofuran is incorrect; and (3) that the nuclear substituted *hexa*hydrodibenzofurans are in reality substituted *tetra*hydrodibenzofurans.

Nuclear substitution of dibenzofuran strikingly illustrates that the rule of conservation of the substitution type is not inviolate, and that the position assumed by substituents is significantly dependent on the kind of entering group. For example, with dibenzofuran, halogenation, sulfonation and the Friedel–Crafts reaction involve the 2-position; nitration involves predominantly the 3-position with only a small amount of 2-nitro compound being formed; and metalation (the replacement of hydrogen attached to carbon by a metal) takes place in the 4-position. With 1,2,3,4-tetrahydrodibenzofuran, sulfonation, the Friedel–Crafts reaction and nitration involve the 7-(or 3′-)position; whereas metalation proceeds as with dibenzofuran to give a 6-(or 4′-) organometallic compound. Bromination may be difficult because bromine is at this time a reagent of choice for dehydrogenation of tetrahydrodibenzofurans to dibenzofurans.

The position of the nitro group in nitro-1,2,3,4-tetrahydrodibenzofuran was established as follows



Ebel[1] nitrated tetrahydrodibenzofuran and assumed that the nitro group was in the 8-position. Von Braun[2] assumed that his nitration product was 8-nitro-*hexa*hydidibenzofuran. Through the kindness of Professor von Braun it was possible to show that a sample of his nitro compound was in reality the 7-nitro-1,2,3,4-*tetra*hydrodibenzofuran. The 8-position assigned to nuclear substituents by these earlier workers was predicated on the reasonable assumption of a *para*-orienting effect of oxygen.

The constitution of the sulfonation product as 1,2,3,4-tetrahydrodibenzofuran-7-sulfonic acid was established by the following sequence of reactions:

$$\begin{tikzcd}
C_{12}H_{12}O\text{ (tetrahydrodibenzofuran)} \arrow[d] & C_{12}H_8O\text{ (dibenzofuran)} \arrow[d] \\
7\text{-}(SO_3H)(C_{12}H_{11}O) \arrow[dd] & 3\text{-}(NO_2)(C_{12}H_7O) \arrow[d] \\
 & 3\text{-}(NH_2)(R) \arrow[d] \\
7\text{-}(SO_2Cl)(C_{12}H_{11}O) \arrow[d] & 3\text{-}(N_2X)(R) \arrow[d] \\
7\text{-}(SO_2NH_2)(C_{12}H_{11}O) \arrow[dd] & 3\text{-}(SO_2H)(R) \arrow[d] \\
 & 3\text{-}(SO_3H)(R) \arrow[d] \\
7\text{-(or 3-)}(SO_2NH_2)(C_{12}H_7O) & 3\text{-}(SO_2Cl)(R) \arrow[l]
\end{tikzcd}$$

A related procedure was used to identify the acetyl compound obtained by a Friedel–Crafts reaction:

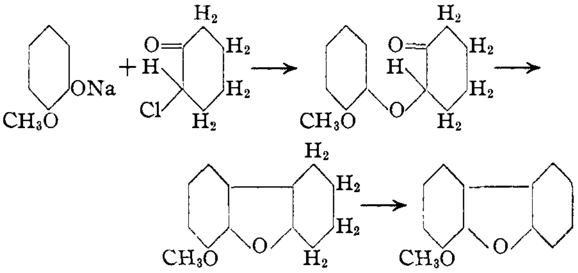
$$7\text{-}(CH_3CO)(C_{12}H_{11}O) \xrightarrow{I_2 + NaOH} 7\text{-}(CO_2H)(C_{12}H_{11}O) \xrightarrow[Br_2]{-4H} 7\text{- (or 3-)}(CO_2H)(C_{12}H_7O)$$

The 7-acetyl-1,2,3,4-*tetra*hydrodibenzofuran was shown to be identical with a supposed 8-acetyl-*hexa*hydrodibenzofuran.[2]

Metalation of *tetra*hydrodibenzofuran by means of phenyl-lithium or *p*-tolyl-lithium or *n*-butylsodium replaced a 6-hydrogen.

$$C_{12}H_{12}O \longrightarrow (C_{12}H_{11}O)(\text{Li or Na}) \xrightarrow{CO_2} (C_{12}H_{11}O)(CO_2H) \xrightarrow[Br_2]{-4H} 6\text{-(or 4-)}C_{12}H_7O(CO_2H)$$

The structure of 6-methoxy-1,2,3,4-tetrahydrodibenzofuran, prepared by the following interesting ring closure synthesis,[1] has been definitely established by dehydrogenation to 4-methoxydibenzofuran which in turn was made available by the recent unequivocal synthesis involving the metalation of dibenzofuran.[3]



An account of some reduction products of dibenzofuran is contained in the Experimental Part.

The pharmacological action of the several compounds will be reported by Dr. A. W. Dox and co-workers.

Experimental Part

1,2,3,4-Tetrahydrodibenzofuran.—The tetrahydrodibenzofuran used in all of the procedures, except when otherwise noted, was prepared according to the directions of Hönigschmid.[4] In a typical preparation 50 g. of dibenzofuran was reduced with 60 g. of sodium, a total of 400 cc. of absolute ethanol being used. The product was purified by distillation at atmospheric pressure, b. p. 270° (740 mm.), followed by a second distillation at reduced pressure, b. p. 145° (15 mm.), 135° (9 mm.), n^{20}_D 1.5795, sp. g.$^{20}_{20}$ 1.0938.

The reduction of 50 g. of dibenzofuran with 20 g. of sodium in boiling ethanol gave 25.7 g. of product distilling between 265–273° (740 mm.), and 15.4 g. boiling at 273–275° (740 mm.). Chilling the second fraction in an ice-salt bath yielded 3.6 g. of crystalline product which melted at 40–45° after one crystallization from ethanol. Several crystallizations from petroleum ether raised the melting point to 80° and this compound was shown to be dibenzofuran.

Nitration of Tetrahydrodibenzofuran.—Nitration by the method of Ebel[1] gave a nitro compound which melted at 124–125° when crystallized from ethanol. The material used was prepared both by ring closure and sodium-ethanol reduction. The compound was identical with the supposed 8-nitrohexahydrodibenzofuran[2] (mixed melting point). This substantiates Ebel's[1] surmise that his nitrotetrahydro compound was probably the same as von Braun's nitrohexahydro compound.

Anal. Calcd. for $C_{12}H_{11}O_3N$: C, 66.33; H, 5.11. Found: C, 66.02; H, 5.23.

A solution of 2.2 g. (0.01 mole) of the nitrotetrahydrodibenzofuran and 3.2 g. (0.02 mole) of bromine in 40 cc. of

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(1) Ebel, *Helv. Chim. Acta*, **12**, 3 (1929).

(2) Von Braun, *Ber.*, **55**, 3761 (1922).

(3) Gilman and Young, THIS JOURNAL, **57**, 1121 (1935).

(4) Hönigschmid, *Monatsh.*, **22**, 561 (1901), and **23**, 829 (1902).

glacial acetic acid was allowed to stand for fifteen hours at room temperature and then refluxed for one-half hour. On cooling, 0.75 g. or a 35% yield of 3-nitrodibenzofuran precipitated (mixed melting point).

The amine and the picrate of the amine prepared by reduction of 7-nitro-1,2,3,4-tetrahydrodibenzofuran were found by Mr. W. H. Kirkpatrick to have the same melting points as the reported amino-hexahydrodibenzofuran and its picrate, respectively.[2] However, the 7-acetamino-1,2,3,4-tetrahydrodibenzofuran was found to melt at 146° and not at 123°, which is the melting point reported for the acetamino-hexahydrodibenzofuran.[2] It is possible that the latter substance, for which no analysis was reported, is a mixture of mono-acetamino and di-acetamino compounds (acylation having introduced two acetyl groups).

Anal. Calcd. for $C_{14}H_{15}O_2N$: N, 6.11. Found: N, 6.31.

Friedel–Crafts Reaction.—The acetylation of tetrahydrodibenzofuran with acetyl chloride and aluminum chloride in carbon disulfide by Mr. J. A. V. Turck yielded an acetyltetrahydrodibenzofuran. The use of acetic anhydride and stannic chloride in benzene proved to be a better choice of reagents and gave the same product. Twenty and four-tenths grams (0.2 mole) of acetic anhydride was added dropwise with stirring to a solution of 34.4 g. (0.2 mole) of tetrahydrodibenzofuran and 104.4 g. (0.4 mole) of anhydrous stannic chloride in 150 cc. of dry benzene. At the conclusion of the addition the mixture was refluxed gently for ten hours and then hydrolyzed with cracked ice. The mixture was extracted with ether, the ether–benzene extract washed with 10% sodium hydroxide and then with water, and, finally, dried over anhydrous calcium chloride. The solvents were removed and the residue fractionated at reduced pressure. The fraction boiling at 200–217° (15 mm.) weighed 28.3 g., or a 66% yield. The solidified product crystallized from petroleum ether as colorless needles, m. p. 66–67°, b. p. 210° (15 mm.). A mixed melting point with an authentic sample of acetylhexahydrodibenzofuran[2] kindly supplied by Professor von Braun, and melting at 66–67°, showed no depression.

Anal. Calcd. for $C_{14}H_{14}O_2$: C, 78.46; H, 6.59. Found: C, 78.46 and 78.44; H, 6.25 and 6.74.

Dibenzofuran was also isolated from the reaction product.

The acetyl derivative supplied by Professor von Braun was also analyzed.

Anal. Calcd. for $C_{14}H_{14}O_2$: C, 78.46; H, 6.59. Calcd. for $C_{14}H_{16}O_2$: C, 77.73; H, 7.46. Found: C, 78.14; H, 6.64.

An aqueous solution of iodine in potassium iodide was added in small portions with shaking to a solution of 4 g. of acetyltetrahydrodibenzofuran in 100 cc. of dioxane and 40 cc. of 10% sodium hydroxide solution in accordance with Fuson's procedure. When the iodine color persisted at 60° for one minute, excess sodium hydroxide was added and the solution cooled. The supernatant liquid was decanted from the iodoform and acidified with sulfuric acid. The resulting precipitate was filtered and then washed. A 2.3 g. or 57% yield of 1,2,3,4-tetrahydrodibenzofuran-7-carboxylic acid was obtained which melted at 247–248° after crystallization from ethanol or glacial acetic acid. *Neutral equivalent:* calcd., 216.1; found, 213 and 213.

Anal. Calcd. for $C_{13}H_{12}O_3$: C, 72.19; H, 5.60. Found: C, 72.07 and 71.90; H, 5.64 and 5.61.

Diazomethane was used to prepare the methyl ester, which melted at 72.5–73.5° after crystallization from dilute methanol.

One and six-tenths grams (0.01 mole) of bromine was added to a suspension of 1.08 g. (0.005 mole) of the above tetrahydrodibenzofuran-7-carboxylic acid in 25 cc. of glacial acetic acid at room temperature and the resulting solution was allowed to stand for ten hours. The solution was refluxed strongly until the evolution of hydrogen bromide ceased, and then cooled. A quantitative yield of dibenzofuran-3-carboxylic acid was obtained which melted at 271.5–272° after crystallization from glacial acetic acid. A mixed melting point with authentic dibenzofuran-3-carboxylic acid, m. p. 271.5–272°, showed no depression.

Diazomethane was used to convert the acid to the methyl ester which melted at 138.5° after crystallization from petroleum ether. A mixed melting point with authentic methyl dibenzofuran-3-carboxylate showed no depression. The methyl ester was prepared by the action of diazomethane on dibenzofuran-3-carboxylic acid, and melted at 138° after crystallization from petroleum ether.

Anal. Calcd. for $C_{14}H_{10}O_3$: C, 74.31; H, 4.46. Found: C, 74.31 and 74.67; H, 4.85 and 4.93.

Sulfonation of Tetrahydrodibenzofuran.—To a well-stirred solution of 34.4 g. (0.2 mole) of tetrahydrodibenzofuran in 100 cc. of carbon tetrachloride was added dropwise 23.4 g. (0.2 mole) of chlorosulfonic acid. The temperature was kept at 10°. At the conclusion of the addition the reaction was stirred for one hour at 0° and at room temperature for three hours. The reaction product was decomposed with cracked ice and the carbon tetrachloride layer separated. The aqueous layer was neutralized in the usual manner with barium carbonate and the slightly soluble barium sulfonate extracted with hot water. Concentration and cooling of the aqueous extract yielded 23.3 g. or a 36.3% yield of barium 1,2,3,4-tetrahydrodibenzofuran-7-sulfonate. The salt was crystallized several times from water prior to analysis.

Anal. Calcd. for $(C_{12}H_{11}O_4S)_2Ba$: Ba, 21.48. Found: Ba, 21.30 and 21.68.

On the basis of the formation of isomers in nuclear substitution reactions of partially reduced related systems, it is not at all unlikely that isomers may have formed in nuclear substitution reactions of 1,2,3,4-tetrahydrodibenzofuran.

Tetrahydrodibenzofuransulfonamide.—An intimate mixture of 21.5 g. (0.0785 mole) of crude sodium tetrahydrodibenzofuransulfonate and 12.3 g. (0.08 mole) of phosphorus oxychloride was allowed to stand for twenty-four hours at room temperature and then heated for one and one-half hours at 100–110°. The pasty reaction product was decomposed with cold concentrated ammonium hydroxide. The solid product was digested with fresh ammonium hydroxide and filtered to give a yield of 77%. The colorless flat plates melted at 207.5–208.5° after crystallization from ethanol and 60% acetic acid.

Anal. Calcd. for $C_{12}H_{13}O_3NS$: C, 57.33; H, 5.21. Found: C, 57.09; H, 4.92.

Dehydrogenation of Tetrahydrodibenzofuransulfonamide.—A solution of 1.28 g. (0.008 mole) of bromine and 1 g. (0.004 mole) of 1,2,3,4-tetrahydrodibenzofuran-7-sulfonamide in 25 cc. of glacial acetic acid was allowed to stand at room temperature for two days and then refluxed until the evolution of hydrogen bromide ceased. The chilled solution precipitated 0.55 g. of dibenzofuran-3-sulfonamide, which gave compact colorless crystals melting at 241–243° after crystallization from 60% acetic acid. A 10% yield of the same product was obtained when 1 g. of tetrahydrodibenzofuransulfonamide and 2 g. of sulfur was heated at 240–275° until evolution of hydrogen sulfide ceased. The product was extracted with and crystallized from 60% acetic acid. A mixed melting point of this compound with the authentic dibenzofuran-3-sulfonamide as prepared by the following sequence of reactions was not depressed.

Dibenzofuran-3-sulfonamide.—A solution of 4.4 g. of sodium nitrite in 20 cc. of water was added slowly to a suspension of 10 g. of 3-aminodibenzofuran in a solution of 40 cc. of concd. sulfuric acid in 150 cc. of water at 0°. The reaction mixture was stirred for one hour at 0° and allowed to stand at room temperature for twelve hours. The diazonium sulfate was saturated with sulfur dioxide at $-5°$, and then 40 g. of copper powder added in portions with vigorous stirring, the temperature being maintained at $-5°$. The resulting sludge was filtered off when the reaction was complete and both filtrate and precipitate were thoroughly extracted with ether. The ether extract, containing the sulfinic acid, was extracted several times with 6 *N* potassium hydroxide. The potassium sulfinate was immediately oxidized with permanganate in the usual manner to the potassium sulfonate which separated from the filtrate of the oxidation solution upon concentration and cooling. The yield of dry product was 10.2 g. or 65.3%, and the free acid was prepared by the acidification of an aqueous solution of this salt. Dibenzofuran-3-sulfonic acid sinters without melting; it was crystallized several times from water and oven-dried prior to analysis.

Anal. Calcd. for $C_{12}H_8O_4S$: S, 12.92. Found: S, 12.58 and 12.67.

An intimate mixture of 2.4 g. of potassium dibenzofuran-3-sulfonate and 5 g. of phosphorus pentachloride generated a considerable amount of heat and soon liquefied. The liquid was poured upon cracked ice, and the resulting precipitate melted at 148.5° after crystallization from benzene and petroleum ether.

Anal. Calcd. for $C_{12}H_7O_3ClS$: C, 54.02; H, 2.65. Found: C, 54.41; H, 2.91.

An ether solution of dibenzofuran-3-sulfonyl chloride was saturated with ammonia gas to yield dibenzofuran-3-sulfonamide melting at 241–242° after crystallization from 60% acetic acid.

Anal. Calcd. for $C_{12}H_9O_3NS$: C, 58.27; H, 3.67. Found: C, 57.87; H, 3.61.

Metalation of Tetrahydrodibenzofuran.—In this reaction it was necessary to use pure tetrahydrodibenzofuran prepared by ring closure.[1] Tetrahydrodibenzofuran prepared by the sodium–alcohol reduction of dibenzofuran contains sufficient impurity to cause the formation of 4-dibenzofurancarboxylic acid, which made isolation of the tetrahydrodibenzofurancarboxylic acid difficult. In a typical preparation, 0.5 mole of phenyl-lithium was prepared in the customary manner[5] from 7.6 g. of lithium, 78.5 g. (0.5 mole) of bromobenzene and 300 cc. of anhydrous ether. This preparation, after removal of the excess lithium, was gently refluxed with a solution of 86.0 g. (0.5 mole) of tetrahydrodibenzofuran in 200 cc. of anhydrous ether for fifteen hours. Carbonation was effected by slowly pouring the cooled reaction product on 500 g. of pulverized solid carbon dioxide. The mixture was allowed to stand overnight and was then extracted with two liters of water made alkaline with sodium hydroxide. Steam distillation of the ether layer resulted in the recovery of 41.4 g. of tetrahydrodibenzofuran. Acidification of the aqueous alkaline extract after decolorization with Norite yielded 18.1 g. of a resinous material. Crystallization of this product from ethyl acetate yielded 2.7 g. of crude 1,2,3,4-tetrahydrodibenzofuran-6-carboxylic acid which melted at 197° after further crystallization from the same solvent. This is a 4.8% yield based on the tetrahydrodibenzofuran used. *Neutral equivalent:* Calcd., 216.1; found, 216.8.

Anal. Calcd. for $C_{13}H_{12}O_3$: C, 72.19; H, 5.60. Found: C, 71.92; H, 5.75.

The use of *p*-tolyl-lithium and *n*-butylsodium as metalating agents yields the same product, but in smaller yields. Metalations of substituted dibenzofurans will be reported later. Depending on the kind and position of substituents, it is possible to metalate in positions other than 4 and 6.

Dehydrogenation of 1,2,3,4-Tetrahydrodibenzofuran-6-carboxylic Acid.—A solution of 0.4 g. (0.00185 mole) of tetrahydrodibenzofurancarboxylic acid and 0.65 g. (0.004 mole) of bromine in 10 cc. glacial acetic acid was allowed to stand overnight at room temperature and then refluxed until the evolution of hydrogen bromide ceased. The solution was diluted to 250 cc., made alkaline with sodium hydroxide, decolorized with Norite and acidified. Dibenzofuran-4-carboxylic acid melting at 207–208° was obtained after crystallization of the resulting precipitate from ethanol. A mixed melting point with authentic dibenzofuran-4-carboxylic acid showed no depression.

In this connection, it is interesting to observe that the reduction of dibenzofuran-4-carboxylic acid by sodium and absolute ethanol gives a reduced acid which appears to be 1,2,3,4-tetrahydrodibenzofuran-4-carboxylic acid. The exact structure of this compound together with others prepared by reduction of substituted dibenzofurans will be described in a forthcoming article. This tetrahydro acid melts at 168° after crystallization from dilute acetone from which the acid separates as large silvery plates. *Neutral equivalent:* Calcd., 216.1; found, 216.3.

Anal. Calcd. for $C_{13}H_{12}O_3$: C, 72.19; H, 5.60. Found: C, 71.89 and 72.42; H, 5.66 and 5.67.

Dehydrogenation of 1,2,3,4-Tetrahydro-6-methoxydibenzofuran.—An intimate mixture of 0.25 g. of the methoxytetrahydro compound[1] and 0.3 g. of sulfur was heated up to 275° until the evolution of hydrogen sulfide

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[5] Gilman, Zoellner and Selby, THIS JOURNAL, **54**, 1957 (1932).

ceased. The solid melt was extracted with hot petroleum ether and the solvent evaporated to dryness. The residue was extracted with cold absolute ethanol and the extract concentrated to yield 4-methoxydibenzofuran[3] (mixed melting point).

Reduced Dibenzofurans.—There appears to be some confusion concerning variously reduced dibenzofurans. The 1,2,3,4-tetrahydrodibenzofuran was first prepared by Hönigschmid[4] by reduction of dibenzofuran with sodium in boiling ethyl or amyl alcohol. Extensive treatment with sodium and amyl alcohol did not yield a more completely reduced product, and when a lesser amount of sodium was used Hönigschmid isolated a compound melting at 43° which he assumed to be dihydrodibenzofuran. We repeated the work and obtained the same product melting at about 43°. However, several crystallizations from ethanol and petroleum ether raised the melting point to 80° and the compound as obtained was shown to be dibenzofuran.

The tetrahydrodibenzofuran has also been prepared by reduction of dibenzofuran with sodium and cyclohexanol.[6]

An entirely different procedure was used by Ebel,[1] who synthesized the tetrahydrodibenzofuran by a ring-closure reaction using 2-chlorocyclohexanone and sodium phenolate. This reaction together with oxidation of the tetrahydro compound to δ-(*o*-hydroxybenzoyl)-valeric acid leaves no doubt as to the constitution of the compound.

The hexahydrodibenzofuran of von Braun[2] was prepared by the catalytic reduction of *o*-biphenol. Ebel[1] introduced two atoms of hydrogen into tetrahydrodibenzofuran, using platinum–palladium black as a catalyst, and obtained a compound whose analysis and boiling point agreed with that of von Braun's hexahydrodibenzofuran.

We have found, however, that the picrates obtained from von Braun's hexahydrodibenzofuran, from Ebel's reduction product of the tetrahydrodibenzofuran and from the tetrahydrodibenzofurans prepared both by Ebel's and Hönigschmid's methods are identical, on the basis of mixed melting points.

The picrates were all prepared in the same manner and melted at 97–98° after crystallization from ethanol.[7] There were significant differences in yields of the picrates prepared from the variously reduced dibenzofurans. Incidentally, it might be added that the picrate prepared from von Braun's hexahydrodibenzofuran was decomposed by steam distillation of a suspension in sodium carbonate solution to yield a compound distilling at 145° (15 mm.) and having an index of refraction (1.5795 at 20°) identical with that observed with the tetrahydrodibenzofuran prepared by sodium reduction.

A dodecahydrodibenzofuran was described recently.[8] Mr. C. W. Bradley prepared this perhydrodibenzofuran by catalytic reduction of dibenzofuran at moderate temperatures and pressures using noble metal catalysts: b. p. 258–259° (740 mm.) and 108–110° (7 mm.); n^{20}_{D} 1 .5023; sp. g. $^{20}_{20}$ 1.0312.

Anal. Calcd. for $C_{12}H_{20}O$: C, 79.93, H, 11.19. Found: C, 80.37; H, 11.19.

An experiment by him to introduce 4 or 6 atoms of hydrogen by this method gave a product from which only dibenzofuran and perhydrodibenzofuran have so far been isolated. Mention should be made of the fact that hydrogenation of 2-hydroxydibenzofuran by Mr. Bradley also gave perhydrodibenzofuran.

The reduced dibenzofurans have been oxidized, von Braun obtaining δ-(*o*-hydroxybenzoyl)-valeric acid from his hexahydrodibenzofuran and chromic acid, and Ebel obtaining the same acid by ozonization of tetrahydrodibenzofuran. Mr. Bradley got a 16.7% yield of the acid by ozonizing the hexahydrodibenzofuran obtained in accordance with Ebel's directions for the reduction of tetrahydrodibenzofuran, an 87% yield of the same acid on ozonization under corresponding conditions of 1,2,3,4-tetrahydrodibenzofuran, and ozonization of the perhydrodibenzofuran gave an as yet unidentified product which is partly soluble in alkali.

From present evidence, there is no doubt concerning the existence of tetrahydrodibenzofuran and the perhydrodibenzofuran. No dihydrodibenzofuran has been definitely established.[7] The hexahydrodibenzofuran presents a different problem. This compound may be known as a parent type, but it seems quite clear that nuclear substitution reactions of it produce tetrahydro derivatives. The removal of two hydrogens from the hexahydro is not surprising with reagents like bromine, nitric acid, ozone and aluminum chloride. Possibly the picric acid also behaves as an oxidizing agent, and if so this would account for the apparent identity of the picrates prepared from the tetra- and hexahydrodibenzofurans.

The authors gratefully acknowledge the assistance of Mr. H. Oatfield with part of the sulfonation experiments and of Mr. W. Hoehn with some of the analyses.

Summary

A study has been made of variously substituted reduced dibenzofurans.

Metalation and nitration of 1,2,3,4-tetrahydrodibenzofuran involve the same relative positions observed with dibenzofuran. However, sulfonation and acetylation take place in the 7-(or 3′-) position, rather than in the 8-(or 2′-) position as in the case with dibenzofuran.

Some substituted *hexa*hydrodibenzofurans reported earlier have been shown to be substituted *tetra*hydrodibenzofurans, the substituents being in the 7- and not in the 8-position as assumed previously.

AMES, IOWA RECEIVED JULY 19, 1935

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(6) Mayer and Krieger, *Ber.*, **55**, 1659 (1922). Cullinane and Padfield [*J. Chem. Soc.*, 1131 (1935)] have just reported the preparation of the tetrahydro compound in 97% yield by reduction of dibenzofuran using platinum black as a catalyst.

(7) Both Ebel and Hönigschmid report the picrate as melting at 91°. Also Cullinane and Padfield [*J. Chem. Soc.*, 1131 (1935)] have just reported a melting point of 91°.

(8) Stenger, German Patent 566,782 [*C. A.*, **27**, 2459 (1933)].