[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Dibenzofuran. II. Metalation

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Introduction

The term metalation is proposed for reactions involving replacement of hydrogen by a metal to give a true organometallic compound. Accordingly, it is related to common substitution reactions such as halogenation, nitration and sulfonation, and as a general expression it includes the special case of mercuration.

As a rule, metalation is commonly observed with nuclei having enhanced aromatic characteristics.¹ Direct comparisons with benzene having revealed the greater aromaticity of dibenzofuran, it was to be expected that dibenzofuran would undergo relatively ready metalation. This is the case, and metalations were effected by metals, organometallic compounds and salts. However, it was surprising to note that metalation occurred in the 4-position, inasmuch as uni-nuclear substitution has hitherto involved exclusively the 2and 3-positions and there has been no authenticated case of substitution in either the 1-position or the 4-position.²

We know now that the rule of conservation of the substitution type is not inviolate and that the position assumed by substituents is dependent not only on the elements or groups already attached to the nucleus and on experimental conditions, but also on the kind of entering group. This is particularly the case with mercuration,³ and an apt illustration is the mercuration of p-nitrotoluene. Coffey^{3a} has shown that mercuration of p-nitrotoluene introduces a mercuri group ortho to nitro to the extent of 77.5% and ortho to methyl to the extent of 22.5%, whereas generally nuclear substitution reactions of p-nitrotoluene go exclusively ortho to methyl. The results described in this and in the preceding paper illustrate very strikingly the effect of the entering group: metalation taking place in the 4-position, nitration in the 3-position, and sulfonation and halogenation in the 2-position. If metalation is

largely a function of relative acidities,⁴ then hydrogen in the 4-position of dibenzofuran is more acidic than hydrogen in the 1- or 2- or 3-position. This remains to be established. This concept may be serviceable in affording a basis for interpreting anomalous substitutions in mercuration, as well as for determining the more acidic hydrogens in both simple and substituted nuclei. Incidentally, it may afford a means of arranging organometallic compounds in a series of relative reactivities.

The yields of metalation products, in some cases, are highly satisfactory, and the general reaction is at this time one of choice for the introduction of substituents in the 4-position. The constitution of the organolithium, -sodium and -potassium compounds was established by conversion by carbonation to 4-dibenzofuran-carboxylic acid, the structure of which was unequivocally demonstrated recently by Kruber.⁵ The 4-dibenzofurylmercuric acetate was first converted to the iodo compound, which in turn readily formed a Grignard reagent which was then carbonated.



Experimental Part

Preparation of Mercurials.—A melt of 16.8 g. (0.1 mole) of dibenzofuran and 23.9 g. (0.075 mole) of mercuric acetate was heated at 150° for 3.5 hours; cooled; the solid, after grinding to a fine powder, was extracted with benzene; and the residue extracted with hot *n*-propyl alcohol to give, on cooling, 17.9 g. or a 56% yield of 4-dibenzofurylmercuric acetate, which after two crystallizations from propyl alcohol and two crystallizations from acetic acid gave 12 g. of mercurial melting at 199–200°.

Anal. Calcd. for $C_{14}H_{10}O_8Hg$: Hg, 47.02. Found: Hg, 48.1, 47.6 and 47.7.

⁽¹⁾ Gilman and Breuer, THIS JOURNAL, 56, 1123 (1934).

⁽²⁾ The small amount of isomeric mono-nitration compound is supposed to be 4-nitrodibenzofuran [Borsche and Schacke, Ber., 56, 2498 (1923); Cullinane, J. Chem. Soc., 2269 (1930)]. However, as will be shown in a subsequent report this is 2-nitrodibenzofuran.

^{(3) (}a) Coffey, J. Chem. Soc., 3215 (1926). See Coffey, Chem. Weekblad, 23, 194 (1926), for a review with pertinent literature citations.

⁽⁴⁾ Conant and Wheland, THIS JOURNAL, 54, 1212 (1932), and Gilman and Breuer, *ibid.*, 56, 1123 (1934).

⁽⁵⁾ Kruber, Ber., 65, 1382 (1932). The authors are grateful to Dr. O. Kruber for a specimen of the 4-dibenzofurancarboxylic acid.

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A lesser yield was obtained by heating at $130-140^{\circ}$ for two hours. The mercurial can also be prepared by mercurating in acetic acid for six hours at the reflux temperature. An insoluble residue appears to be dibenzofuryl-4,?-dimercuric acetate which decomposes at about 315° and analyzes 3.5% too high for mercury in a dimercurial.

4-Dibenzofurylmercuric chloride is precipitated immediately when an alcoholic calcium chloride solution is added to a warm *n*-propyl alcohol solution of 4-dibenzofurylmercuric acetate, and can be purified by dissolving in acetone and precipitating with water to give a product melting at $235-238^{\circ}$.

Reactions of 4-DibenzofuryImercuric Acetate.—Cleavage of 1 g. of the mercurial in propyl alcohol by hydrogen chloride gave 0.3 g. or an 81% yield of dibenzofuran.

4-Iododibenzofuran was prepared in a 30% yield by the addition of iodine in methanol to a suspension of the mercurial in ethanol, and it melts at $71-72^{\circ}$ after thrice crystallizing from methanol.

Anal. Calcd. for $C_{12}H_7OI$: I, 43.2. Found: I, 43.6, 43.8 and 43.55.

4-Dibenzofurylmagnesium iodide was readily prepared in the customary manner from 0.7 g. (0.0024 mole) of 4iododibenzofuran. The Grignard reagent gives a positive color test,⁶ and when carbonated by solid carbon dioxide⁷ yielded 0.2 g. or 36% of 4-dibenzofurancarboxylic acid. The acid melted at 208–209°, after crystallization from ethanol, and showed no depression in melting point when admixed with an authentic sample kindly provided by Dr. Kruber.

4-Iododibenzofuran is reduced to dibenzofuran by the action of magnesium and hydrochloric acid.

4-Dibenzofuryl-lithium.—A mixture of dibenzofuran and methyl-lithium in ether was sealed in a Schlenk tube under nitrogen and set aside at room temperature for two weeks. There was considerable pressure, probably of methane, on opening the tube. Carbonation with solid carbon dioxide gave 4-dibenzofurancarboxylic acid. Metalation by methyl-lithium can also be effected in conventional reaction flasks provided only with a trap⁸ to exclude moisture and air. In this case it was observed that no appreciable quantity of 4-dibenzofuryl-lithium was formed at the end of fifteen hours as evidenced by the non-appearance of 4-dibenzofurancarboxylic acid when an aliquot was removed and carbonated. However, an aliquot removed at the end of forty hours gave the carboxylic acid on carbonation. **4-Dibenzofurylsodium.**—A mixture of 16.8 g. (0.1 mole) of dibenzofuran, 2.3 g. (0.1 atom) of sodium cut in small pieces, 10 g. (0.0032 mole) of di-*n*-butylmercury and 60 cc. of petroleum ether (b. p., $68-70^{\circ}$) was sealed in a nitrogen-filled Schlenk tube which was shaken for two days and then allowed to stand for ten days. The color test was positive, and carbonation with solid carbon dioxide gave 4.75 g. or a 36% yield of 4-dibenzofurau-carboxylic acid. The sodium salt of the acid is only slightly soluble in water.

In another experiment, the reactants were shaken for three days and then allowed to stand at room temperature for two days, to yield 40% of the acid after carbonation. In a third preparation, the reactants were shaken for four days and then allowed to stand for nineteen days to give a 58% yield of acid. The 4-dibenzofurancarboxylic acid obtained in this manner is relatively pure, for the crude material melts at 207–208° and one crystallization from alcohol gives the pure acid melting at 209°.

4-Dibenzofurylpotassium.—In a corresponding experiment, sodium-potassium alloy, dibenzofuran and petroleum ether were sealed in a nitrogen filled tube which was shaken for three days and then allowed to stand for eight days at room temperature. Reaction developed at once, and a brown precipitate formed. Carbonation with solid carbon dioxide gave a small amount of 4-dibenzofurancarboxylic acid (mixed m. p.), and the products of carbonation were not examined for other acids.

Summary

Metalation (the replacement of hydrogen by metal to give an organometallic compound) of dibenzofuran gives the 4-dibenzofurylmercuri -lithium, -sodium and -potassium compounds.

This is the first authenticated case of substitution in the 4-position and, when considered with nitration that occurs in the 3-position, and halogenation and sulfonation which occur in the 2position, strikingly illustrates that the rule of conservation of the substitution type is not inviolate and that the position assumed by substituents is dependent not only on the elements and groups attached to the nucleus and on experimental conditions, but also on the kind of entering group.

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⁽⁶⁾ THIS JOURNAL, 47, 2002 (1925).

⁽⁷⁾ Ibid., 55, 1258 (1933).

⁽⁸⁾ Rec. trav. chim., 48, 1124 (1929).