

g. γ -lactone in 13.4041 g. H_2O , heated for five hours on a boiling water bath and cooled quickly gave $[\alpha]_D^{20} = -58.79^\circ$, *i. e.*, $\alpha = -2.75^\circ$ in a 1 dc. tube; curiously enough the specific rotation rose after 16 hours' standing at room temperatures to -59.87° . (C) A third experiment with 0.5035 g. γ -lactone in 11.9932 g. H_2O , heated on a boiling water bath for seven hours and cooled quickly, gave $[\alpha]_D^{20} = -59.54^\circ$, *i. e.*, $\alpha = -2.67^\circ$ in a 1 dc. tube. Here again a curious rise and subsequent fall in specific rotation were observed on standing at ordinary temperatures.

Time after first reading.	Observed angle.	$[\alpha]_D$.
19 hrs.	-2.77°	-61.77°
6 days	-2.54°	-56.63°

It is clear from the data presented that aqueous solutions of ortho-bis-*d*-galactonic acid, or of *d*-galactonic γ -lactone or its hydrate, finally come to an equilibrium at 20° with $[\alpha]_D^{20} = -48.5^\circ$; at 100° , on the other hand, equilibrium is quickly reached with $[\alpha]_D^{20} = -60^\circ$. Such solutions contain 17 to 37% of free *d*-galactonic acid and 83 to 63% of *d*-galactonic γ -lactone hydrate (besides traces of γ -lactone) according to the temperature (between 20° and 100°) at which equilibrium occurs.

One might also draw the conclusion from the slight fluctuations at first noticed in the specific rotation of ortho-bis-*d*-galactonic acid, or of free *d*-galactonic acid when set free from its salts, as well as the curious fluctuations in specific rotation noticed after aqueous solutions of ortho-bis-*d*-galactonic acid and of *d*-galactonic γ -lactone have been heated at 100° and quickly cooled, that a faintly dextrorotatory *d*-galactonic β -lactone also exists in these solutions. All attempts, however, to isolate such a β -lactone, or even an ester of *d*-galactonic acid, were entirely fruitless.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

SYNTHESES IN THE DIPHENYLMETHANE SERIES.

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The work presented in this paper was undertaken with the idea of attempting to effect a synthesis of the hydrocarbon, fluorene, through the action of metals upon 2,2'-dibromodiphenylmethane. This latter substance was prepared by the elimination of the amino groups from 3,3'-diamino-6,6'-dibromodiphenylmethane, a compound which, in turn, had

¹ The work described in this article formed part of a thesis submitted for the degree of Master of Science to the graduate school of the University of Illinois by E. A. Wildman.

been obtained by acetylation and subsequent bromination of 3,3'-diaminodiphenylmethane.

In marked contrast to the usual ease with which, under the influence of sodium or other metals, ring formation occurs in the case of organic compounds halogenated in the 1,5-position, is the behavior of 2,2'-dibromodiphenylmethane under similar circumstances. Although sodium was allowed to act upon the dibromodiphenylmethane, both in anhydrous ether solution and in boiling xylene, and although the substance was subjected to the action of other metals, such as copper in the form of "Naturkupfer," and magnesium at temperatures up to 260°, the bromo-compound was in all cases recovered almost entirely unchanged, the only observed effect of the treatment being a slight reduction to diphenylmethane.

An interesting case of steric hindrance is observable in the behavior of hydroxylamine or of semicarbazine towards 2,2'-dibromobenzophenone, obtained by the oxidation of 2,2'-dibromodiphenylmethane. In the case of the former of these reagents several hours' boiling of the solution was insufficient to involve the ketone in reaction; and after being exposed to the action of semicarbazine for a month the ketone was recovered unchanged from the solution.

Experimental.

***m*-Nitrobenzyl Alcohol.**—In general the method of Becker¹ was followed, wherein *m*-nitrobenzaldehyde was subjected to the action of potassium hydroxide, in accordance with the well-known reaction of Cannizzaro. It was found advantageous, however, to saturate the alkaline solution with carbon dioxide before extracting the alcohol with ether. Under these circumstances the yield amounts to 92% of the theoretical.

3,3'-Dinitrodiphenylmethane.—This substance was first described by Gattermann and Rüdts² who prepared it by the condensation of *m*-nitrobenzylalcohol with nitrobenzene in the presence of sulfuric acid. In the same year, M. Schöpf obtained the compound through the action of formaldehyde upon nitrobenzene in sulfuric acid solution. Baeyer,⁴ employing, with slight modifications, the method of Gattermann and Rüdts, prepared the substance in 25% yield, the amount of tarry material formed at the same time being considerable.

At first, in our attempts to improve the yield by changing the conditions of condensation, 10 g. of *m*-nitrobenzylalcohol and 30 g. of nitrobenzene were dissolved in 200 cc. of concentrated sulfuric acid, and the solution allowed to remain at room temperature for 72 hrs. After the reaction mixture had been poured upon cracked ice it was observed that the amount

¹ *Ber.*, 15, 2090 (1882).

² *Ibid.*, 27, 2295 (1894).

³ *Ibid.*, 27, 2321 (1894).

⁴ *Ann.*, 354, 192 (1907).

of tarry material formed was negligible; hence it was unnecessary to purify the product by means of acetone, as recommended by Baeyer. The yield amounted to 20% of the theoretical.

Again, upon allowing the mixture to stand at room temperature for eleven days, the quantity of tar formed was very small, while the yield was increased to 25%.

After the solution of nitrobenzyl alcohol and nitrobenzene had remained on the water bath at a temperature of 95–97° for six hrs., the yield amounted to only 14%, while a similar treatment for 18 hrs. gave a 20% yield.

Finally, after 48 hrs. at a temperature of 95–97°, the yield increased to 30%, the amount of tarry material being very slight. Accordingly, these conditions were adopted for the preparation of 3,3'-dinitrodiphenylmethane.

3,3'-Diaminodiphenylmethane.—This base was first prepared by M. Schöpf¹ from the corresponding dinitro-compound by reduction with stannous chloride. The yield, however, was poor. Better results were obtained with metallic iron and acetic acid.

Fourteen grams of 3,3'-dinitrodiphenylmethane were mixed in a porcelain dish with 30 g. of iron, in the form of powder, and 50 cc. of water. Two cubic centimeters of glacial acetic acid were added, and the mixture was then heated on the water bath, with constant stirring, until the reaction was apparently at an end. After about 2 hrs. further heating the greater part of the water had evaporated. The base was extracted with ether, the ethereal solution dried over potassium hydroxide, and the ether distilled. The product, which was obtained as a viscous oil, was immediately converted into its acetyl derivative.

3,3'-Diacetylaminodiphenylmethane.—The diamine, obtained as described above, was dissolved in 20 cc. of glacial acetic acid, and 15 cc. of acetic anhydride were added to the solution. Heat was evolved, and the reaction was brought to completion by warming the solution to its boiling point. The acetyl derivative, which separated in crystalline condition upon pouring the reaction mixture into cold water, was filtered with the aid of suction, and recrystallized from dilute alcohol. The yield was 13 g. or 83% of the theoretical, based upon the nitro compound.

3,3'-Diacetylaminodiphenylmethane crystallizes in the form of colorless leaflets, and has a melting point of 193°. It is readily soluble in alcohol or glacial acetic acid; slightly soluble in ether, benzene or ligroin; very slightly soluble in water.

0.2897 g. substance: 25.9 cc. N₂ (26°, 745 mm., over KOH).

Calc. for C₁₇H₁₈O₂N₂: N, 9.82; found: 9.90%.

3,3'-Diacetyl-amino-6,6'-dibromodiphenylmethane.—Twenty grams of 3,3'-diacetylaminodiphenylmethane were dissolved in 500 cc. of glacial

¹ *Ber.*, 27, 2322 (1894).

acetic acid, and to the solution, maintained at a temperature of 50° and constantly stirred, 17 g. of bromine were gradually added. Fumes of hydrogen bromide were evolved. The mixture was allowed to stand for a short time, and then poured into four times its volume of cold water. The product was filtered at the pump, and washed with cold water. Yield, 26 g., or 84% of the theoretical.

3,3'-Diacetylamino-6,6'-dibromodiphenylmethane crystallizes in the form of small, colorless plates from glacial acetic acid, in which it is fairly soluble, or from alcohol, in which it is only slightly soluble. It is very difficultly soluble in ether, benzene, ligroin or carbon tetrachloride. The melting point is 284°.

0.2987 g. subs. required 27.1 cc. 0.05 *N* AgNO₃; 0.2964 g. gave 17.0 cc. N₂ (25°, 753 mm. over KOH).

Calc. for C₁₇H₁₆O₂N₂Br₂: Br, 36.34; N, 6.36; found: Br, 36.25%; N, 6.40%.

3,3'-Diamino-6,6'-dibromodiphenylmethane.—Sixty grams of the diacetyl compound and 250 cc. of alcohol were placed in a flask, provided with a reflux condenser. The mixture was heated to boiling, and then 200 cc. of hydrochloric acid (sp. gr. 1.19) were added gradually. After half an hour's heating saponification was complete, and the solution entirely clear. Soon the hydrochloride of the base began to crystallize out in the form of fine, colorless needles. At this point boiling was discontinued and the solution allowed to cool. The product was filtered off, and washed with alcohol, the greater part of the impurities remaining in the mother liquor. The latter was evaporated almost to dryness on the water bath, ammonia added, and the base extracted with ether. From the ethereal solution the almost pure salt was precipitated by means of hydrogen chloride.

When an aqueous solution of the hydrochloride is treated with ammonia the base is precipitated as an oil which soon solidifies to a mass of crystals, easily soluble in ether, alcohol or glacial acetic acid. After several recrystallizations from alcohol the substance showed a melting point of 114°. The base is rather unstable as, upon exposure to the air, it quickly turns brown.

On account of the instability of the free base it was decided to analyze the sulfate, since this salt was found to be only slightly soluble in cold water, and could easily be purified by recrystallization from this medium.

0.2983 g. subs. gave 14.1 cc. N₂ (20°, 746 mm.); 0.4602 g. subs. required 33.2 cc. 0.05 *N* AgNO₃.

Calc. for C₁₃H₁₂N₂Br₂·(H₂SO₄)₂: N, 5.07; Br, 29.02; found: N, 5.27; Br, 28.82.

A sample of the hydrochloride was titrated against standard potassium hydroxide solution, with phenolphthalein as indicator.

Calc. for C₁₃H₁₂N₂Br₂·2HCl: HCl, 17.40; found: 17.20.

2,2'-Dibromodiphenylmethane.—This substance was prepared by replacing in 3,3'-diamino-6,6'-dibromodiphenylmethane the amino groups

with hydrogen. Several unsuccessful attempts were made to eliminate the amino groups before a satisfactory method was found. Thus, neither the diazotization of the hydrochloride of the base by means of amyl nitrite in alcoholic solution, nor the reduction of the diazonium compound with sodium stannite, nor the oxidation of the corresponding hydrazine with copper sulfate or with potassium chromate led to satisfactory results. The procedure outlined below furnishes, however, a fairly good yield of 2,2'-dibromodiphenylmethane.

Ten grams of the hydrochloride of the base were made into a paste with 30 cc. of water and 10 cc. of hydrochloric acid (1.19). The mixture was maintained at a temperature of 0° while a cold, saturated solution of sodium nitrite was slowly added until a test with starch-iodide paper indicated free nitrous acid, the presence of a slight excess of which was found desirable since the salt diazotized somewhat slowly. When the mixture had become entirely homogeneous it was poured into one liter of boiling alcohol. A brisk evolution of nitrogen followed. The alcohol was distilled, and the remaining light brown oil taken up with ether. After the ethereal solution had been dried over calcium chloride, and the solvent removed, the residue was distilled under a pressure of 45 mm. The yield was 6.5 g. of a pale yellow, heavy liquid which came over between 220 and 245°. In an attempt to further purify the substance by distillation under 5 mm. pressure, a nearly colorless fraction was obtained between 212 and 218°. It seemed to be a mixture, however, and this supposition was confirmed by analysis.

0.2536 and 0.1403 g. subs. required 29.4 and 16.3 cc. 0.05 *N* AgNO₃.

Calc. for C₁₃H₁₀Br₂: Br, 49.04; found: 46.32 and 46.42.

Since the bromine content was low it was supposed that the impurity might be the ethoxy derivative which might have been formed as a by-product in the decomposition of the diazonium salt by the alcohol. Accordingly, 12 g. of the distillate were shaken with 40 cc. of concentrated sulfuric acid, and the insoluble portion which rose to the surface of the acid was separated, and distilled under 40 mm. A colorless liquid, boiling constantly at 234–235° was collected.

0.1419 g. subs. required 17.2 cc. 0.05 *N* AgNO₃.

Calc. for C₁₃H₁₀Br₂: Br, 49.04; found: 48.44.

The indices of refraction and dispersion were determined by means of an Abbé refractometer.

$$N_D(20^\circ) = 1.6300$$

$$N_F - N_C(20^\circ) = 0.0213$$

$$\text{Specific gravity: } D_4^{20} = 1.6197.$$

Action of Metals upon 2,2'-Dibromodiphenylmethane.—A solution of 10 g. of 2,2'-dibromodiphenylmethane in 150 cc. of anhydrous ether was treated with a slight excess of sodium wire, and the mixture allowed to

remain at room temperature for 24 hrs. After filtration and distillation of the ether, the original bromo compound was recovered unchanged.

Two grams of 2,2'-dibromodiphenylmethane and an excess of sodium wire were added to 50 cc. of anhydrous xylene, and the solution maintained at the boiling point for 6 hrs. Except for a slight reduction to diphenylmethane, due probably to a trace of moisture, there was no apparent action.

Two grams of the bromo compound, together with 2 g. of copper bronze, were heated to a temperature of 260° for several hours, according to the method of Ullmann. The original compound was recovered unchanged.

In the same manner, and with similar results, 2 g. of 2,2'-dibromodiphenylmethane with 2 g. of powdered magnesium and a trace of iodine were maintained at a temperature of 260° for one hour.

2,2'-Dibromodiphenylketone.—Five grams of 2,2'-dibromodiphenylmethane were dissolved in 50 cc. of glacial acetic acid. Ten grams of chromic anhydride in saturated aqueous solution were added, and the mixture heated on the water bath for six hours. The solution was then poured into ten times its volume of water, and the ketone extracted with ether. The acetic acid was removed from the ethereal extract by shaking with dilute potassium hydroxide solution. After drying over anhydrous sodium sulfate, and distillation of the ether, a colorless oil remained. A few cubic centimeters of alcohol were added to the oil, and the mixture stirred, whereupon the ketone was obtained as a crystalline mass. From its alcoholic solution the substance separates in the form of beautiful, hexagonal plates, melting at 86°.

2,2'-Dibromobenzophenone is insoluble in water; readily soluble in ether, acetone, chloroform, carbon tetrachloride, hot glacial acetic acid or hot alcohol.

0.3067 g. subs. required 35.6 cc. 0.05 *N* AgNO₃.

Calc. for C₁₂H₈OBr₂: Br, 47.02; found: 46.38.

In an attempt to prepare the oxime, equivalent quantities of ketone, hydroxylamine sulfate and potassium hydroxide in dilute alcoholic solution were heated for eight hours under a reflux condenser. Water was then added, and the mixture extracted with ether. From the ethereal solution the ketone was recovered unchanged.

In the same way, attempts to prepare the semicarbazone yielded negative results, even though the solution was allowed to stand for a month.

Oximes of analogously constituted ketones have never been prepared, owing probably to steric hindrance. Under very energetic treatment a Beckmann rearrangement may take place. If one of the substituents in the ortho position is a halogen atom another type of reaction may occur under the influence of alkali: formation of a five-membered heterocyclic compound of the isoxazole type.