Summary

γ-Benzoyl-γ-butyrolactone and α-hydroxy-δ-benzoylvaleric acid have been synthesized. The latter has been identified with the end-product obtained by degradation of the compound obtained by the ring closure of 1,4-dibromo-1,4-dibenzoylbutane. This result confirms the identification of this compound as 2-phenyl-3-cyano-6-benzoyl-5,6-dihydro-1,4-pyran.

URBANA, ILL. RECEIVED OCTOBER 16, 1933

[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

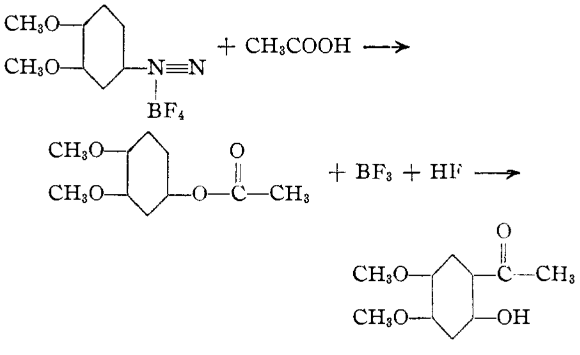
The Action of Acetic Acid on 3,4-Dimethoxyphenyldiazonium Borofluoride

BY L. E. SMITH AND H. L. HALLER

It has been shown recently[1] that acetic acid interacts with *m*-chlorophenyldiazonium borofluoride to give *m*-chlorophenyl acetate in a yield of about 50%. As the acetate is readily saponified to the phenol, the method appeared to be useful for the preparation of phenols when the normal decomposition of the diazo compound in water does not take place readily. Accordingly, the reaction suggested itself for the preparation of 1-hydroxy-3,4-dimethoxybenzene, a degradation product of rotenone and related substances, that is obtained only in poor yield through the usual diazo reaction on veratrylamine.

When this reaction was carried out, instead of yielding the expected acetate of 1-hydroxy-3,4-dimethoxybenzene, it yielded a product of the same empirical formula as the desired acetate, but soluble in alkali. This product contained two methoxyl groups, yielded an oxime and a semicarbazone, and with dimethyl sulfate and sodium hydroxide it was methylated to give an alkali-insoluble product. On oxidation with an aqueous solution of potassium permanganate the methylated product gave a keto acid, which on treatment with hydrogen peroxide yielded asaronic acid.

These reactions identified the original compound as a hydroxydimethoxyacetophenone, and its melting point and the melting points of its derivatives showed it to be identical with 2-hydroxy-4,5-dimethoxyacetophenone. The formation of this substance can be accounted for by the assumption that the acetate which is first formed is rearranged by the boron fluoride produced in the reaction. The exact mechanism of the reaction is not known, but the following is suggested.



Boron fluoride has been shown to rearrange alkyl phenyl ethers to the isomeric nuclei substituted phenols,[2] but the writers found no record of boron fluoride producing a wandering of an acyl group. However, the wandering of an acyl group under the influence of aluminum chloride is well known. The solid product obtained was homogeneous, and there was no evidence that a methyl group had migrated.

In addition to the 2-hydroxy-4,5-dimethoxyacetophenone, there was obtained a small quantity of a fluorine compound which contained two methoxyl groups. It is probably 3,4-dimethoxyfluorobenzene.

Experimental Part

Veratrylamine.—Veratrol was nitrated by the method of Cardwell and Robinson.[3] The yield was 99% of the theoretical. The nitroveratrol was suspended in ethyl alcohol at 50° and reduced with hydrogen, platinum oxide being used as a catalyst. The reduction proceeded rapidly with the evolution of sufficient heat to keep the solution warm. When the absorption of hydrogen had ceased, the solution was filtered from the catalyst into alcohol containing the theoretical amount of hydrochloric acid. The alcoholic solution was then concentrated to a small volume under reduced pressure, ether was added, and the

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[1] Haller and Schaffer, THIS JOURNAL, **55**, 4954 (1933).

[2] Sowa, Hinton and Nieuwland, *ibid.*, **54**, 2019 (1932); *ibid.*, **55**, 3402 (1933).

[3] Cardwell and Robinson, *J. Chem. Soc.*, **107**, 257 (1915).

amine hydrochloride was filtered off and dried. The yield was quantitative.

In addition to giving a better yield, this procedure is much more convenient than is the reduction with tin and hydrochloric acid or with sodium sulfide.

3,4-Dimethoxyphenyldiazonium Borofluoride. — This compound was obtained from diazotized veratrylamine and fluoboric acid by the general procedure of Balz and Schiemann.[4] Nineteen grams of the amine hydrochloride yielded 20 g. of the diazonium borofluoride (76%). The salt was soluble in acetone, and insoluble in benzene and in chloroform. It was recrystallized by dissolving 5 g. of the salt in 30 cc. of acetone, heating the solution to boiling, and then adding 20 cc. of benzene. It melted with decomposition at 123°.

Anal. Calcd. for $C_8H_9N_2O_2BF_4$: OCH_3(2), 24.6. Found: OCH_3, 24.5.

2 - Hydroxy - 4,5 - dimethoxyacetophenone.—Twenty-five grams of 3,4-dimethoxyphenyldiazonium borofluoride suspended in 125 cc. of glacial acetic acid was heated under a reflux condenser until nitrogen evolution was evident. The borofluoride went into solution, and after the vigorous reaction which took place had subsided the solution was refluxed for ten minutes; it was then cooled, and the product which separated was filtered off. It contained boron and fluorine, which were gradually lost on heating the product. The yield was 13.5 g. The crude product was dissolved by heating it in 250 cc. of 15% potassium hydroxide solution. The hot solution was filtered through charcoal, cooled and then acidified. The precipitate was filtered off, washed with water and dried. Twelve grams of substance was obtained. It was recrystallized from 40% alcohol; it can also be recrystallized from toluene. It melted at 112°, which agrees with the melting point previously recorded.[5]

Anal. Calcd. for $C_{10}H_{12}O_4$: C, 61.22; H, 6.12; OCH_3 (2), 31.63. Found: C, 60.92; H, 6.0; OCH_3, 31.30.

The acetic acid filtrate was concentrated under reduced pressure to a small volume. The precipitate was filtered off and combined with the first crop of crystals. The mother liquor was neutralized with 20% potassium hydroxide solution; the precipitate was filtered off, and the alkaline solution was extracted with ether. The ether extract was washed with water and dried over sodium sulfate. After removal of the ether the residual oil was distilled. It boiled at 98° (14 mm.). It is in all probability 3,4-dimethoxyfluorobenzene.

Anal. Calcd. for $C_8H_9O_2F$: OCH_3(2), 39.74; F, 12.18. Found: OCH_3, 39.44; F, 12.2.

2-Hydroxy-4,5-dimethoxyacetophenone Oxime.—One gram of the substituted acetophenone, 0.35 g. of hydroxylamine hydrochloride and 0.7 g. of sodium acetate in 15 cc. of ethyl alcohol were refluxed for seven hours. On cooling, the crystals were filtered off, washed with water and dried; yield, 0.3 g. The product melted at 161–162°. The filtrate was heated to boiling and diluted with an equal volume of water. On cooling, 0.65 g. of oxime was obtained The melting point was 162°. From the mother liquor an additional 0.1 g. of oxime, which also melted at 162°, was obtained. The combined product was recrystallized from 10% alcohol. The melting point was 162°.

Anal. Calcd. for $C_{10}H_{13}O_4N$: N, 6.63; OCH_3 (2), 29.37. Found: N, 6.53; OCH_3, 29.7

2-Acetyl-4,5-dimethoxyacetophenone.[5]—One gram of 2-hydroxy-4,5-dimethoxyacetophenone was acetylated with acetic anhydride and sodium acetate in the usual manner. The acetyl derivative was recrystallized from dilute ethyl alcohol. It melted at 147°, which agrees with the melting point recorded. The yield was 0.85 g.

2,4,5-Trimethoxyacetophenone.[6]—To a cold solution of 6 g. of 2-hydroxy-4,5-dimethoxyacetophenone in 80 cc. of 5% potassium hydroxide solution, 7.5 g. of dimethyl sulfate was added slowly with constant mechanical stirring. After one hour the crystalline precipitate was filtered off and dissolved in ether. The ether solution was extracted with 5% potassium hydroxide solution, then washed with water and dried over sodium sulfate. The ether was removed, and the remaining substance was recrystallized from 30% alcohol. It can also be crystallized from toluene. It melted at 99°. The yield was 4 g.

Anal. Calcd. for $C_{11}H_{14}O_4$: OCH_3(3), 44.28. Found: OCH_3, 44.04.

From the alkaline solution 1.9 g. of unchanged material was recovered.

2,4,5-Trimethoxyacetophenone Semicarbazone.—To 0.6 g. of the trimethoxyacetophenone in 10 cc. of ethyl alcohol was added a solution of 0.6 g. of semicarbazide hydrochloride and 0.7 g. of sodium acetate in 5 cc. of water. The clear solution was shaken in a mechanical shaker for seven hours and then placed in the ice box overnight. The crystalline product was filtered off, washed with water and recrystallized from 50% alcohol. The yield was 0.65 g. It melted at 206° with previous softening at 200°. Bargellini and Avrutin[7] record a melting point of 186–188°.

Anal. Calcd. for $C_{12}H_{17}O_4N_3$: N,[8] 5.24; OCH_3(3), 34.83. Found: N, 5.39; OCH_3, 35.03.

Oxidation of 2,4,5-Trimethoxyacetophenone to 2,4,5-Trimethoxyphenylglyoxylic Acid.—Two grams of the trimethoxyacetophenone suspended in 100 cc. of hot water was oxidized on the steam-bath by the gradual addition of 3 g. of potassium permanganate. The mixture was cooled, filtered and then extracted with ether. The aqueous solution was acidified with dilute hydrochloric acid and extracted with ether. The ether extract was dried over sodium sulfate. After the ether was removed the remaining substance was recrystallized from benzene. The yield was 0.55 g. It melted at 186°.

Anal.[9] Calcd. for $C_{11}H_{12}O_6$: C, 55.0; H, 5.0; mol. wt., 240. Found: C, 55.07; H, 5.40; mol. wt. (titration), 241.

Oxidation of 2,4,5-Trimethoxyphenylglyoxylic Acid to Asaronic Acid.—Four-tenths gram of the trimethoxyphenylglyoxylic acid was dissolved in 6 cc. of 5% potassium hydroxide solution. The solution was heated to about 60° and 1.5 cc. of 30% hydrogen peroxide was added slowly.

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[4] Balz and Schiemann, *Ber.*, **60**, 1186 (1927).

[5] Bargellini and Aureli, *Atti. accad. Lincei*, **II**, [5] **20**, 118 (1911).

[6] Regrodski and Tambor, *Ber.*, **43**, 1965 (1910).

[7] Bargellini and Avrutin, *Gazz. chim. ital.*, **40**, II, 342 (1910).

[8] Veibel, *Bull. soc. chim.*, [4] **41**, 1410 (1927).

[9] The writers are indebted to Mr. J. R. Spies of this division for the micro combustions.

The solution was finally heated to boiling, then cooled and acidified with dilute hydrochloric acid. The precipitated acid was filtered off and recrystallized from water. It melted at 145°. When mixed with an equal quantity of asaronic acid there was no depression of the melting point.

Summary

The reaction of 3,4-dimethoxyphenyldiazonium borofluoride with acetic acid gives 2-hydroxy-4,5-dimethoxyacetophenone.

Oxidation of 2,4,5-trimethoxyacetophenone by aqueous potassium permanganate yields 2,4,5-trimethoxyphenylglyoxylic acid, which is oxidized to asaronic acid with hydrogen peroxide.

WASHINGTON, D. C. RECEIVED OCTOBER 17, 1933

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

Indirect Hydrolysis of Hexaphenylethane

BY W. E. BACHMANN

We have observed that when a solution of triphenylmethyl and magnesium iodide in a mixture of ether and benzene is poured into water, triphenylmethane and triphenylcarbinol are formed in equivalent amounts. The reaction corresponds to the addition of the elements of water to the radical.

$$2(C_6H_5)_3C + HOH \longrightarrow (C_6H_5)_3CH + (C_6H_5)_3COH \quad (1)$$

However, it is well known that triphenylmethyl in spite of its great reactivity does not react with water.

An explanation for the products seemed to be provided by the reaction reported by Gorski[1] to take place between triphenylmethyl and magnesium iodide; according to him interaction of the two compounds gives a Grignard reagent and iodine. Since the latter would react with triphenylmethyl and give triphenylmethyl iodide, one should expect to get a mixture of carbinol and methane on hydrolysis. In support of his formulation Gorski reported that an excellent yield of triphenylacetic acid is obtained when carbon dioxide is passed through a mixture of magnesium iodide and triphenylmethyl in ether and benzene.[2] We have repeated the reaction of Gorski and we have found that the reported reaction does not take place. We passed carbon dioxide through a solution of magnesium iodide and triphenylmethyl in ether and benzene at room temperature and at the boiling point of the mixture, for short and for long periods of time; in no case was triphenylacetic acid formed. A reading of the experimental details in Gorski's article showed that he allowed metallic magnesium to remain in the mixture in order to take up the iodine which he wrongly believed was liberated in the reaction. Actually, then, the formation of the Grignard reagent which took place in his experiments was due to the action of the binary system $Mg + MgI_2$[3] on the triphenylmethyl. Indeed, the absence of reaction between triphenylmethyl, magnesium iodide and carbon dioxide confirms the view of Gomberg and Bachmann that the formation of the Grignard reagent from triphenylmethyl takes place by direct addition of MgI to the radical.

The true explanation for the conversion of triphenylmethyl to the corresponding methane and carbinol was found in an observation made during the process of hydrolysis. It was noticed that when the mixture of triphenylmethyl and magnesium iodide comes in contact with the oxygen of the air a deep red-brown color develops and when this mixture is poured into water iodine is liberated. It occurred to us that part of this iodine is taken up by the triphenylmethyl; the triphenylmethyl iodide thus formed is then rapidly hydrolyzed to triphenylcarbinol with liberation of hydrogen iodide. The latter then reacts with triphenylmethyl and gives a mixture of triphenylmethane and triphenylmethyl iodide; hydrolysis of the latter to the carbinol regenerates the hydrogen iodide and the chain reaction continues until all of the radical has been converted to equivalent amounts of the methane and carbinol.

$$\begin{aligned}
&(a)\quad (C_6H_5)_3C + I \longrightarrow (C_6H_5)_3CI\\
&(b)\quad (C_6H_5)_3CI + HOH \longrightarrow (C_6H_5)_3COH + HI\\
&(c)\quad 2(C_6H_5)_3C + HI \longrightarrow (C_6H_5)_3CH + (C_6H_5)_3CI
\end{aligned}$$

If this hypothesis is correct, then it should be possible to convert triphenylmethyl into a mixture of equivalent parts of triphenylmethane and triphenylcarbinol by means of water and a small

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(1) Gorski, *J. Russ. Phys.-Chem. Soc.*, **45**, 1454 (1913).

(2) See Beilstein, fourth ed., Supplement, Vol. IX, p. 309; also *C. A.*, **8**, 325 (1914).

(3) Gomberg and Bachmann, THIS JOURNAL, **49**, 236 (1927).