Several attempts have been made to obtain acetonic acid from this product as Willgerodt did from chloretone, but although a small amount of a supposedly organic acid was obtained and an attempt made to convert it into the barium salt, the amount was so small that the results obtained were not sufficiently close to demonstrate its formation, although it was probable. What has been said relative to chloretone (Cameron and Holly) is no doubt true of brometone, *viz.*, that the substance contains water, and in varying amounts, that the water cannot be detected or eliminated by mechanical means, that it is not present to form a hydrate. Therefore it is present to form a solid solution. Brometone is used as a therapeutic agent. For its pharmacological action see Houghton and Aldrich.[1]

THE REDUCTION OF THE ANHYDROXIME OF *o*-BENZOYLBENZOIC ACID.

BY ROBERT EVSTAFIEFF ROSE.

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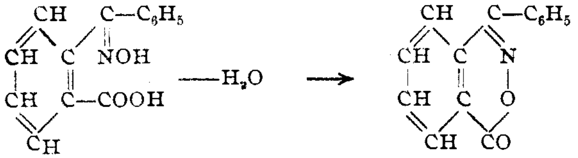
In common with other oximes of aromatic aldehydes and ketones containing a carboxyl group in the *o*-position to the carbonyl that of *o*-benzoylbenzoic acid is incapable of existing in the free state. It loses the elements of water spontaneously when liberated from its alkali salt, yielding what may be termed an anhydroxime thus:



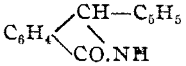
Several representatives of this class of compounds are known, but their chemical behavior has been little studied, though a closely related substance, the oxime of phenolphthalein, has been the subject of thorough investigation. It therefore seemed of interest to examin the behavior of the anhydroxime of *o*-benzoylbenzoic acid more especially towards reducing agents, the analogous compound obtained from phenolphthalein having proved to be readily reducible.

Experiment showed the anhydroxime to undergo quantitative reduction when treated with nascent hydrogen, a stable crystallin reduction product being formed.

For this substance the following formulas must be considered:

I. 

$$C_6H_4\begin{cases}CH_2\text{—}C_6H_5\\ CONH_2\end{cases}$$

II. 

$$C_6H_4\begin{cases}CH\text{—}C_5H_5\\ CO.NH\end{cases}$$

of which the first shows the reduction product as the amide of *o*-benzyl-

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[1] *Am. J. Physiol.* (proceedings), 8, 18 (1903).

benzoic acid, while the second represents the substance as the lactam of the *o*-carbonic acid of diphenylmethylamine. Formula I, though appearing somewhat improbable when compared with that given above for the anhydroxime, deserves consideration because it is analogous to the one originally proposed by R. Meyer[1] for the reduction product of the oxime of phenolphthalein. Study of the behavior of the compound and the analytical results obtained led the author to adopt the alternative formula II as being more closely in accord with the observed facts. Did formula I represent the structure of the substance then as an acid amide it should be capable of undergoing hydrolysis to the corresponding acid; this is not the case. Moreover the percentage difference in carbon and hydrogen in the two compounds amounting as it does to 0.76 per cent. and 0.90 per cent. respectively is quite sufficient to allow of analytical determination, and the values found agree closely with those calculated for the lactam. Again, a substance possessing the constitution represented by formula II should be extremely stable, and the reduction product does, in fact, resist the action of reducing and hydrolyzing agents to a remarkable degree. Thus it dissolves readily in concentrated sulfuric acid from which it is precipitated in an unchanged condition on the addition of water, while if the acid solution is heated sulfonation alone results.

The substance is insoluble in alkalies; behavior which is in conformity with the lactam structure since this represents the compound as being more basic than acidic. As was to be expected the reduction product readily undergoes acetylation, yielding a monoacetyl derivative.

Further evidence is furnished by the behavior of the compound toward reagents for the hydroxyl group. It is itself colorless, but when treated with phosphorus pentachloride, acetyl chloride, or benzoyl chloride yields a dark blue-green, highly fluorescent substance which was not obtained in a state of purity. This change to a highly colored compound can be satisfactorily explained on the assumption that the action of these reagents causes tautomerism to the lactam, the chromophore —C=N— being produced; thus:

The constitution of this product is of interest because of its probable analogy to the corresponding derivative of phenolphthalein oxime which will form the subject of a subsequent paper.

Experimental.

Preparation of the Oxime of o-Benzoylbenzoic Acid.[2]—22.6 grams *o*-benzoyl-

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[1] *Ber.*, 40, 1454.

[2] See Thorpe, *Ber.*, 26, 1262, 1795.

benzoic acid, melting point 93–96°, were dissolved in a .solution of 56 grams potassium hydroxide in 200 cc. water and to this were added 15.75 grams hydroxylamine hydrochloride in concentrated aqueous solution. The reaction mixture was boiled during 20 minutes, allowed to stand 12 hours at room temperature, then acidified with hydrochloric acid; a crystallin mass separated which was recrystallized from ethyl alcohol; melting point 161–163. Yield, 90 per cent.

Reduction of the Anhydroxime.—Ten grams of the substance were dissolved in the minimum quantity of glacial acetic acid and a large excess of zinc dust added in small portions. Slight warming was sufficient to start the reaction after the addition of the first portion of zinc, the remaining metal being thereafter added in such a manner as to keep the mixture near the boiling point. When all the zinc had been added the reaction mixture was allowed to stand for half an hour, then poured into cold water. The product was recrystallized from 75 per cent. acetic acid. It melts at 218–220°, and was found to be rather soluble in methyl and ethyl alcohols, slightly soluble in ether, and insoluble in petroleum ether. Analysis gave the following results:

Found:	C, 80.33, 80.05;	H, 5.29, 5.46;	N, 6.70.
Calculated for $C_{14}H_{11}NO$:	C, 80.38;	H, 5.26;	N, 6.69.

A molecular weight determination in acetic acid by the cryoscopic method gave the value 221 instead of that calculated 209.

Acetylation of the Reduction Product.—Two grams of the compound were dissolved in 30 cc. of acetic anhydride to which 4 grams of anhydrous sodium acetate had been added and the mixture boiled for 6 hours. On pouring the reaction mixture into cold water a solid separated, which, after recrystallization from aqueous acetic acid, melted constantly at 153–155°. Analysis gave:

N, 5.60; calculated for $C_{16}H_{13}O_3N$: N, 5.57.

Sulfonation of the Reduction Product.—In an endeavor to hydrolyze the substance it was treated with concentrated sulfuric acid; it dissolved readily in the acid but was reprecipitated unchanged on dilution. When 5 grams of the compound were dissolved in a large excess of concentrated sulfuric acid and heated for 4 hours at 160–170° sulfonation resulted, and the barium salt of the sulfonic acid was obtained after neutralizing with barium carbonate, filtering and evaporating the aqueous solution. The salt crystallized from water in small prisms containing two molecules of water of hydration. Analysis gave the following results:

Found:	H_2O, 4.24;	Ba, 18.26.
Calculated for $(C_{14}H_{10}O_4NS)_2Ba.2H_2O$:	H_2O, 4.25;	Ba, 18.29.

Action of Benzoyl Chloride and Acetyl Chloride on the Reduction Product.—No satisfactory results were obtained by the use of these reagents; in every case the reaction mixture became dark blue-green in color with the formation of a substance far more soluble in ether and benzene than the original compound. It is proposed to examin this reaction further.

Distillation of the Reduction Product with Zinc Dust.—An attempt was made to reduce the substance still further by distilling with zinc dust, this method having been used by v. Baeyer in converting oxindole into indole; as a result an oily mixture of substances was obtained from which colorless leaflets separated which were found to be carbazole. The oily substance formed at the same time showed most intense blue-red fluorescence but was present in quantities too small to admit of identification.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF SWARTHMORE COLLEGE.]

THE ACTION OF ETHYL ALCOHOL ON PARATOLUIDINE DIAZONIUM HYDROCHLORIDE AND OF SULFURIC ACID ON THE ETHYL ETHER OF PARACRESOL.

BY PERCIVAL RUDOLPH ROBERTS AND GELLERT ALLEMAN.

Received January 2, 1911.

Some years ago, one of us[1] studied the action of methyl alcohol on paratoluidine diazonium sulfate and the effect of sulfuric acid on the methyl ether of paracresol. It was thought that the ethyl ether of paracresol could be obtained in a like manner, and with no more difficulty than attended the preparation of the corresponding methoxy compound. Numerous failures to secure a good yield of the ethoxy product led to changes in the methods and conditions incident to the production of the material desired. Owing to the fact that paratoluidine sulfate is much less soluble in ethyl alcohol than is paratoluidine hydrochloride, the latter compound was employed.

Preparation of the Diazonium Compound.—Two hundred grams of Kahlbaum's paratoluidine were melted in 400 cc. of hot water, and 400 cc. of fuming hydrochloric acid gradually added. During the addition of the acid, the mixture was stirred in order to dissolve the hydrochloride formed. As soon as complete solution took place, the material was cooled by immersing the beaker containing it in cold water. The paratoluidine hydrochloride separated, on cooling, in perfectly white crystals. The supernatant liquid was decanted, the crystals thrown on a funnel fitted with a platinum cone, and the adhering water and acid removed by filtering under diminished pressure. The crystals were then placed on an unglazed porcelain plate to facilitate drying. They were used within an hour of the time they were removed from the liquid, because the color of the crystals changed, on standing over night, which indicated that, within a short time, some decomposition resulted. The crystals, which

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[1] Alleman, *Am. Chem. J.*, 31, 24 (1904).