hydrolysis takes place and a portion of the cystine precipitates out in the form of hexagonal plates. That hydrolysis had not taken place in preparing the saturated solution is clearly shown by the very close agreement between solubilities calculated from contents of nitrogen and sulfur on the one hand and barium on the other.

When the dry salt was heated in a melting point tube it showed no signs of decomposition or fusion up to about 250°; then it began to brown very gradually but without sintering.

When a portion of the salt equivalent to 2.5 g. of cystine was refluxed with 50 cc. of distilled water for twelve hours, nitrogen and sulfur analyses made after the removal of free hydrogen sulfide and ammonia indicated that decomposition to the extent of approximately 50% had taken place.

In its property of being water soluble, the barium salt of *l*-cystine resembles the alkali salts and differs from the heavy metal salts so far described. This characteristic as well as its ease of preparation and the ease of determination of its metallic constituent should make the barium salt useful in further studies on the mechanism of the alkaline decomposition of cystine. It might also find use in the preparation of derivatives of cystine, particularly in cases where the reaction requires anhydrous conditions.

CONTRIBUTION FROM THE
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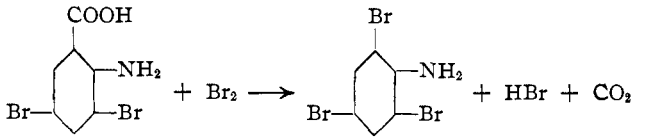
The Structure of the Bromination Product of Ortho-Nitrotoluene

BY DAVID L. YABROFF

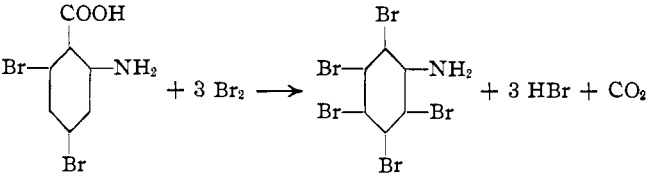
Wachendorff[1] obtained a dibromo product upon the bromination of *o*-nitrotoluene which he called a dibromonitrotoluene. He made the observation, however, that this product was soluble in alkali. Greiff[2] showed that the compound was a dibromo-anthranilic acid and suggested that it might be the *p-m*-dibromo-anthranilic acid obtained by Hübner[3] upon the nitration and reduction of *p-m*-dibromobenzoic acid since both of the products melted at 225°.

If an intramolecular oxidation and reduction of the nitrotoluene occurs before the bromination, we should expect 3,5-dibromo-2-aminobenzoic acid as the final product. If bromination occurs before the oxidation–reduction process, we should expect 4,6-dibromo-2-aminobenzoic acid to be formed. These two compounds may be readily distinguished by allowing them to react for twenty-four hours in a dilute alcoholic solution with bromine water in the presence of a mineral acid. Under these conditions[4,5] all positions ortho or para to the amino group which are not already substituted are brominated, and at the same time bromine is substituted for the carboxyl group. This may be represented as

[1] Wachendorff, *Ann.*, **185**, 259 (1877).
[2] Greiff, *Ber.*, **13**, 288 (1880).
[3] Hübner, *ibid.*, **10**, 1706 (1877).
[4] Francis and Hill, THIS JOURNAL, **46**, 2498 (1924).
[5] Flürscheim and Holmes, *J. Chem. Soc.*, 448 (1928).



Oxidation–reduction occurring first



Bromination occurring first

In one case we would obtain tribromoaniline, in the other case pentabromoaniline. The product actually obtained by this treatment was tribromoaniline—m. p. 119°, mixed m. p. 120°; bromine analysis (Carius),[6] found 72.3, 72.2%; calcd. for $C_6H_2NH_2Br_3$: 72.7.

These results indicate that the oxidation–reduction process of the nitrotoluene occurs first and the anthranilic acid formed is then brominated, giving rise to the 3,5-dibromo-2-aminobenzoic acid. Wheeler and Oates[7] obtained this compound (m. p. 232°) by the direct bromination of anthranilic acid.

[6] These analyses were carried out by Mr. Leslie H. Bayley.

[7] Wheeler and Oates, THIS JOURNAL, **32**, 770 (1910).

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The Isomeric Desoxybenzanisoins

BY JOHANNES S. BUCK AND WALTER S. IDE

In a recent paper[1] S. S. Jenkins criticizes some of our work,[2] being apparently unable to reproduce certain of our results. The Friedel and Crafts reaction which is in question goes unusually well, and we have repeated the other two questioned preparations, with results identical to those which we reported previously.

We desire to correct Jenkins' statement that, with regard to the reduction of benzanisoin to *p*-methoxybenzyl phenyl ketone, we reported none of the isomeric ketone. On the contrary we specifically stated[3] that isomeric ketones might be present but that no serious attempt to isolate these was made. Jenkins neglects to mention that we proved the structure of our compounds by the Beckmann reaction. His work

[1] Jenkins, THIS JOURNAL, **54**, 1155 (1932).

[2] Buck and Ide, *ibid.*, **53**, 1536 (1931).

[3] Ref. 2, p. 1538.