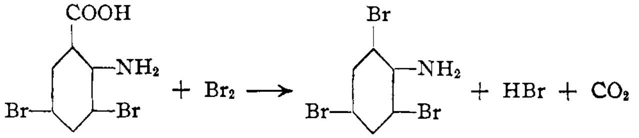
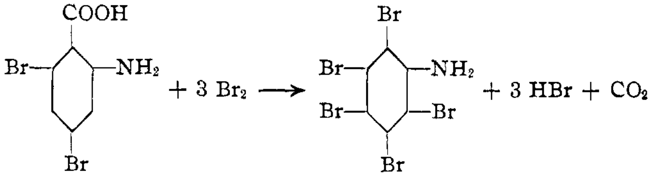


Oxidation–reduction occurring first



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

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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.

has not contradicted any of our conclusions as to the structures of the compounds obtained by us.

In view of the difficulties which have arisen, we submit descriptions of the methods of preparation in question at greater length. The preparations have been checked, and we reaffirm our earlier statements.

Benzyl *p*-Methoxyphenyl Ketone.—15.5 g. of phenylacetyl chloride[4] and 13.0 g. of anisole (calcd. 10.8) were dissolved in 100 cc. of carbon bisulfide (Baker c. p.), in a flask fitted with a reflux condenser and a wide tube for adding the aluminum chloride; 15.0 g. of powdered aluminum chloride (Baker, anhydrous, c. p.) was then added in portions over thirty minutes. The bisulfide refluxes gently during the addition, and hydrogen chloride is evolved. The mixture becomes deep crimson in color and a dark crimson oil sinks to the bottom. After standing at room temperature for a further ninety minutes, 150 g. of crushed ice was added and then 20 cc. of concd. hydrochloric acid. The bisulfide layer was separated and washed twice with dilute hydrochloric acid (further bisulfide being added if the product starts to separate). The bisulfide was then evaporated on the steam-bath, 100 cc. of water added and steam bubbled through for ten minutes. On cooling the product solidified, and was then filtered off, washed with water, drained and dissolved in hot alcohol. On standing the ketone crystallized out. The melting point was 72°, raised to 74–75° on recrystallization. On three consecutive runs the yields were 19.4, 18.3 and 19.0 g., average, 84%. A further quantity (about 1.5 g.) may be obtained on diluting the liquors. Washing with alkali is unnecessary.

***p*-Methoxybenzyl Phenyl Ketone.**—50.0 g. of benzanisoin was dissolved in 200 cc. of 96% alcohol, in a flask fitted with a reflux condenser; 50.0 g. of mossy tin and 50.0 cc. of concd. hydrochloric acid were added, together with 0.5 g. of copper sulfate. The mixture was refluxed on the steam-bath for twelve to fifteen hours, a little (0.5 g.) copper sulfate being added occasionally as the reaction slowed down. After the first six hours, an additional 50 cc. of concd. hydrochloric acid was added to the mixture. When the reaction was complete, the mixture was filtered hot, the product rapidly crystallizing out on cooling. After standing, it was filtered off and washed with water, and then with cold alcohol; yield (unrecrystallized) 87%. Recrystallized from alcohol, the product melted at 91–92° and weighed 37.7 g. (82%). The melting point is raised to 94° after two further recrystallizations. The writers were unable to obtain a pure specimen of benzyl *p*-methoxyphenyl ketone from the liquors of this preparation.

Oximes of *p*-Methoxybenzyl Phenyl Ketone.—14.4 g. of *p*-methoxybenzyl phenyl ketone was dissolved in 100 cc. alcohol (96%) and hydroxylamine acetate solution (from 8.0 g. hydroxylamine hydrochloride and 13.0 g. potassium acetate) added. The reaction mixture was kept at 40–50° for two hours, when crystals commenced to separate. The mixture was then put in a cold place (0°) overnight and the crystals which formed were filtered off next day. After one recrystallization from alcohol the melting point was 132°. The liquors, after evaporation under reduced pressure, deposited a product, which, recrystallized several times from alcohol, melted at 95–96° (previously reported as 94°). The yield of the *anti* oxime (m. p. 132°) is about 10 g. and that of the *syn* oxime about 2 g., the relative amounts varying somewhat in different preparations.

Erratum.—In the paper in question,[2] p. 1540, line 19, for "Ketone E" read "Benzoin 5."

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[4] Vanino and Thiele, *Ber.*, **29**, 1727 (1896).