Ethyl 2-Cyano-4′-stilbenecarboxylate.—Hydrolysis of the combined fractions of the imino ether hydrochloride by stirring 13 g. in 100 cc. of water on a steam-bath for one to two hours, gave a suspension of a fluffy white solid, ethyl 2-cyano-4′-stilbenecarboxylate. By recrystallization from alcohol there was obtained 6.2 g. (53%, based on the dinitrile) of colorless needles, m. p. 128.5–129.5°.

Anal. Calcd. for $C_{18}H_{15}NO_2$: C, 78.1; H, 5.4. Found: C, 78.3; H, 5.6.

In an attempt to convert ethyl 2-cyano-4′-stilbenecarboxylate into diethyl 2,4′-stilbenedicarboxylate via the imino ether hydrochloride, over half of the starting material was recovered unchanged. From the mother liquor was obtained a homogeneous white crystalline solid, m. p. 199–200°, containing nitrogen, the compound was not further investigated.

2-Cyano-4′-stilbenecarboxylic Acid.—A solution of 23 g. of 2,4′-dicyanostilbene in a mixture of 50 cc. of water, 150 cc. of glacial acetic acid, and 50 cc. of sulfuric acid, was refluxed with stirring for ten hours. A white solid began to appear after refluxing for one-half hour. The white solid was filtered from the chilled reaction mixture, and a sample was purified by recrystallization from acetic acid or alcohol. There was in this way obtained a good yield of white crystalline 2-cyano-4′-stilbenecarboxylic acid, m. p. 280–281°; neutral equivalent, 243. Theoretical for $C_{16}H_{11}NO_2$, 249.

Anal. Calcd. for $C_{16}H_{11}NO_2$: N, 5.6. Found: N, 5.6.

2,4′-Stilbenedicarboxylic Acid.—A solution of the crude 2-cyano-4′-stilbenecarboxylic acid in 200 cc. of 20% sodium hydroxide was refluxed for eight hours, diluted with three volumes of water and filtered. The white solid, obtained by acidification of the filtrate with hydrochloric acid, was washed with water and recrystallized from glacial acetic acid. There was thus obtained 8.5 g. (32%, based on the dinitrile) of white crystalline dicarboxylic acid, m. p. 295–6°.

Anal. Calcd. for $C_{16}H_{12}O_4$: C, 71.6; H, 4.5. Found: C, 71.4; 4.7.

Diethyl 2,4′-Stilbenedicarboxylate.—A mixture of 2.68 g. (0.01 mole) of 2,4′-stilbenedicarboxylic acid and 0.06 mole of diazoethane (prepared from 10.3 g. of β-N-ethylnitrosoaminoisobutyl methyl ketone) in a mixture of 50 cc. of ether and 50 cc. of dioxane, was let stand overnight. After filtering off a small amount of unchanged acid, the ether was distilled off. The dioxane solution was diluted with water and the oil, which was by this means thrown out of solution, crystallized on chilling. After recrystallization from alcohol, diethyl 2,4′-stilbenedicarboxylate was obtained in clusters of colorless needles, m. p. 67–8°.

Anal. Calcd. for $C_{20}H_{20}O_4$: C, 74.1; H, 6.2. Found: C, 74.1; H, 6.4.

Analytical data were obtained through the courtesy of the late J. T. Bryant.

THE LILLY RESEARCH LABORATORIES
ELI LILLY AND COMPANY
INDIANAPOLIS, INDIANA

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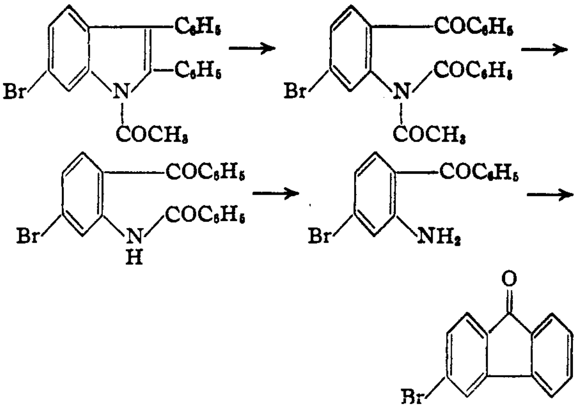
The Bromination of 1-Acetyl-2,3-diphenylindole

BY C. F. KOELSCH

It has been shown[1] that the product obtained by the action of bromine on 1-acetyl-2,3-diphenylindole is either a 4- or a 6-bromo derivative. The transformations illustrated and described in the present note demonstrate that this product is 1-acetyl-6-bromo-2,3-diphenylindole.

The fluorenone obtained melts at 161–162° and therefore is 3-bromofluorenone (m. p. 161°[2]) and not 1-bromofluorenone (m. p. 134–134.3°[3]); the latter would be formed if the starting material were 1-acetyl-4-bromo-2,3-diphenylindole.



2,3-Diphenylindole was obtained in 87% yield by boiling a mixture of 194 g. of benzoin, 300 ml. of aniline, and 50 ml. of concd. hydrochloric acid for two hours.

A solution of 5 g. of 2,3-diphenylindole in 25 ml. of acetone rapidly reduced 2 g. of potassium permanganate at 25–30°; the neutral product separated from benzene in the form of colorless prisms (2.3 g.) that melted[4] with effervescence at 199–200°; this substance has been analyzed but not further investigated.

Anal. Calcd. for $C_{40}H_{28}N_2O + C_6H_6$: C, 87.5; H, 5.4. Found: C, 87.5; H, 5.3.

1-Acetyl-2,3-diphenylindole was obtained in 71% yield when a mixture of 50 g. of 2,3-diphenylindole, 50 g. of dry potassium acetate, and 250 ml. of acetic anhydride was boiled for four hours. Oxidation of the acetyl derivative with chromic acid in acetic acid, followed by prolonged acid hydrolysis of the crude oxidation product, yielded *o*-aminobenzophenone, yellow crystals from alcohol, m. p. 106–108°.

1-Acetyl-6-bromo-2,3-diphenylindole, m. p. 136–139° (reported[1] 141–142°) was obtained in 43% yield by the procedure of Plant and Tomlinson,[1] or in 66% yield when chloroform was used as the solvent for the bromination. In both instances lower melting substances containing bromine were formed, but these could not be purified.

2-(N-Acetyl-N-benzoylamino)-4-bromobenzophenone, colorless prisms from benzene and ligroin, m. p. 138–140°, was obtained in 55% yield when a mixture of 2.7 g. of chromic anhydride in a little water and 7.8 g. of 6-bromo-1-acetyl-2,3-diphenylindole in 80 ml. of acetic acid was allowed to stand for two hours at room temperature and then heated to 70° for a few minutes.

Anal. Calcd. for $C_{22}H_{16}BrNO_3$: C, 62.5; H, 3.8. Found: C, 62.3; H, 4.0.

When the preceding diacyl derivative (1.5 g.) was boiled with 10 ml. of alcohol and 5 ml. of hydrochloric acid for thirty minutes, it was converted into **2-(benzoylamino)-4-bromobenzophenone**; yield, 1.25 g. (93%). The substance formed colorless needles from acetic acid that melted at 147–148°, resolidified at 150°, and remelted at 154–156°.

Anal. Calcd. for $C_{20}H_{14}BrNO_2$: C, 63.2; H, 3.7. Found: C, 63.3, 63.1; H, 3.7, 3.8.

The benzoyl derivative was recovered unchanged after it had been boiled for twenty-four hours with alcoholic hydrochloric acid, but when it was boiled (*ca.* 150°) for three hours with 15 parts of a mixture of equal volumes of sulfuric acid and water, it gave benzoic acid and **2-amino-4-bromobenzophenone** (yield 55%), which formed yellow needles from dilute alcohol, m. p. 88–90°.

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[1] Plant and Tomlinson, *J. Chem. Soc.*, 955 (1933).

[2] Heilbron, Hey and Wilkinson, *ibid.*, 113 (1938).

[3] Huntress, Pfister and Pfister, THIS JOURNAL, **64**, 2845 (1942).

[4] A calibrated thermometer was used in determining the m. p.'s reported in this note.

Anal. Calcd. for $C_{13}H_{10}BrNO$: C, 56.5; H, 3.6. Found: C, 56.3; H, 3.9.

A solution of 0.5 g. of the amino ketone in 10 ml. of dilute hydrochloric acid was treated at 10° with 0.2 g. of sodium nitrite, allowed to stand for ten minutes, and then heated to boiling. The resulting 3-bromofluorenone separated from alcohol in the form of yellow plates (0.3 g.), m. p. 161–162°.

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The Stereochemistry of Coördination Number Eight. Corrections

BY LOUIS E. MARCHI

Attention has been called to several serious errors which appeared in "The Stereochemistry of Coördination Number Eight."[1]

On page 331, in the right hand column, the sixth line from the bottom which reads 3AB CD EF should be deleted, since it is an obvious repetition of the line above it; the seventh line from the bottom should read 2AB CD EF instead of 3AB CD EF, since the latter is not a member of a class of coördination number eight.

In Table IV, page 332, the isomer numbers for Class AB, 6c, Configuration C, should be: Optically active, 0; Optically inactive, 1; Total, 1, instead of Optically active, 2; Optically inactive, 0; Total, 2. In the same table, on page 333, the isomer numbers for Class 3AB 2c, Configuration C, should be: Optically active, 14; Optically inactive, 2; Total, 16, instead of Optically active, 20; Optically inactive, 0; Total, 20.

(1) Marchi, THIS JOURNAL, **65**, 329–333 (1943).

MONSANTO CHEMICAL COMPANY
CENTRAL RESEARCH DEPARTMENT, UNIT III
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The Reaction of Alkyl Halides with Potassium Iodide

BY H. J. MCDONALD, L. R. ROTHSTEIN AND H. E. ROBISON

Conant and Hussey[1] have previously described the reaction between several types of alkyl chlorides and potassium iodide. We have checked some of the results of these investigators and have extended their procedure to certain other alkyl halides.

We have found that there is no measurable reaction between either *t*-amyl chloride or *i*-butyl chloride and potassium iodide after contact times of twenty-four hours at temperatures up to 60°. The result obtained in the former case is not surprising in view of the fact that tertiary alkyl halides in general are extremely unreactive. In such second order substitution reactions, Conant[1] has shown the ease of substitution to be primary > secondary > tertiary.

On this basis it is difficult to see why the primary alkyl halide, *i*-butyl chloride, should prove so unreactive. For although the above-mentioned workers have also shown that branching of the chain reduces reactivity by as much as 100%, their data indicate that *i*-amyl chloride would have reacted with the iodide to an extent of 50% under the same conditions of time and temperature (twenty-four hours and 60°).

The possibility that the *i*-butyl compound might have rearranged during distillation to the more unreactive *t*-butyl chloride was eliminated by refractive index measurements; found, $n^{25}D$ 1.4000; known, $n^{15}D$ 1.40096.[2]

(1) Conant and Hussey, THIS JOURNAL, **47**, 476 (1925).

(2) Timmermans and Martin, *J. chim. phys.*, **23**, 747 (1926).

DEPARTMENT OF CHEMISTRY
ILLINOIS INSTITUTE OF TECHNOLOGY
CHICAGO, ILLINOIS
RECEIVED JULY 17, 1944

3,5-Diiodo-4-(4′-hydroxyphenoxy)-hippuric Acid and 3,5-Diiodo-4-(3′,5′-diiodo-4′-hydroxyphenoxy)-hippuric Acid

BY CARL NIEMANN AND G. E. MCCASLAND

In the course of testing a series of reactions in order to determine their usefulness for the synthesis of thyroxine containing peptides 3,5-diiodo-4-(4′-hydroxyphenoxy)-hippuric acid and 3,5-diiodo-4-(3′,5′-diiodo-4′-hydroxyphenoxy)-hippuric acid have been prepared and characterized.

3,5-Diiodo-4-(4′-acetoxyphenoxy)-benzoic Acid (I).—To 10 g. of recrystallized 3,5-diiodo-4-(4′-hydroxyphenoxy)-benzoic acid,[1] m. p. 259–60°, was added 40 ml. of acetic anhydride and 2–3 drops of concentrated sulfuric acid and the mixture heated at 100° for thirty minutes. The solution was cooled, poured into ice water and, after decomposition of the acetic anhydride, the colorless solid, which had separated, was collected, washed and dried *in vacuo*. The crude product (10.8 g.) was twice recrystallized from absolute ethanol to give 9.6 g. (89%) of I, colorless needles, m. p. 231–232°.

Anal. Calcd. for $C_{15}H_{10}O_5I_2$ (524): C, 34.4; H, 1.9; I, 48.4. Found: C, 34.7; H, 2.1; I, 48.8.

Ethyl 3,5-Diiodo-4-(4′-acetoxyphenoxy)-hippurate (II).—To 3.1 g. of I suspended in 20 ml. of dry benzene was added 1.35 g. of phosphorus pentachloride and the mixture gradually heated to 70°. After cooling to 10° the crystalline acid chloride was collected, at 10°, and washed with 30–60° ligroin. The vacuum dried product weighed 2.7 g. A dry ethereal solution of glycine ethyl ester prepared by the method of Fischer[2] was standardized, by titration with standard acid, and the requisite amount of this solution added to the dry acid chloride and the mixture allowed to stand for sixteen hours at 5°. The solid was collected, washed several times with water and dried *in vacuo* to give 1.7 g. of II, colorless powder, m. p. 144–145°. The ethereal filtrate was washed with water, dilute hydrochloric acid, and again with water and dried first over anhydrous potassium carbonate and finally over Drierite. Evaporation of the dried solution gave an additional 0.7 g. of II for a total yield of 2.4 g. (67%).

Anal. Calcd. for $C_{19}H_{17}O_6NI_2$ (609): C, 37.5; H, 2.8; N, 2.3. Found: C, 37.5; H, 3.0; N, 2.4.

3,5-Diiodo-4-(4′-hydroxyphenoxy)-hippuric Acid Monohydrate (III).—To 2 g. of II was added 40 ml. of 1 *N* sodium hydroxide in 50% ethanol and the suspension

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(1) (a) C. R. Harington and G. Barger, *Biochem. J.*, **21**, 169 (1927); (b) C. Niemann and C. E. Redemann, THIS JOURNAL, **63**, 1549 (1941).

(2) E. Fischer, *Ber.*, **34**, 433 (1901).