added to a quinoline compound containing the trifluoromethyl group.

***m*-Trifluoromethylphenyllithium.**—To a solution of 13.5 g. (0.06 mole) of *m*-trifluoromethylphenyl bromide in 35 cc. of ether cooled by an ice-bath was added with stirring and over a one hour period, a solution of 0.067 mole of *n*-butyllithium in 140 cc. of ether. The solution was stirred at the temperature of the ice-bath for two hours and then allowed to stand for one hour at room temperature. Color test I[4] was strong, and color test II[5] was weak. Carbonation, by pouring on a dry ice–ether slurry, followed by hydrolysis, yielded 7.1 g. (62.2%) of *m*-trifluoromethylbenzoic acid[6] melting at 97.5–99.5°. When the interconversion reaction with *n*-butyllithium was carried out at the reflux temperature of ether, the acid obtained was very impure.

In another preparation under the same conditions, 0.59 mole of *n*-butyllithium in 760 cc. of ether reacted with 130 g. (0.58 mole) of *m*-trifluoromethylphenyl bromide in 200 cc. of ether. This preparation gave a strong color test I and a negative color test II. This solution, in which a 70% yield of the RLi compound was assumed, was used in the following reactions.

2-(*m*-Trifluoromethylphenyl)-quinoline.—A solution of 0.2 mole of *m*-trifluoromethylphenyllithium in 500 cc. of ether was added during one hour to a stirred solution of 25.8 g. (0.2 mole) of quinoline in 50 cc. of ether. After heating at reflux for three hours, the mixture was hydrolyzed by pouring upon 200 g. of ice. The ether layer was separated and mixed with 25 cc. of nitrobenzene. After removal of the ether by distillation, the residue was refluxed gently for twenty minutes. Distillation under reduced pressure gave 37.2 g. (68.2%) of yellowish 2-(*m*-trifluoromethylphenyl)-quinoline which boiled at 142–144° (1–2 mm.), from a bath heated at 172–178°. The compound crystallized after standing at room temperature for several days, and recrystallization from 95% ethanol gave a product melting at 51–52°. The compound is quite soluble in 95% ethanol, methanol, benzene, chloroform, and acetone, but insoluble in 10% hydrochloric acid.

Anal. Calcd. for $C_{16}H_{10}F_3N$: N, 5.13. Found: N, 5.05 and 5.07.

2-(*m*-Trifluoromethylphenyl)-8-methylquinoline.—A solution of 0.2 mole of *m*-trifluoromethylphenyllithium in 500 cc. of ether was added during twenty-five minutes to a stirred solution of 28.6 g. (0.2 mole) of 8-methylquinoline in 50 cc. of ether. The subsequent operations were like those used in the reaction with quinoline, the mixture with nitrobenzene being heated for one hour in a bath at 120°. Distillation at 145–147° (1–2 mm.), from a bath heated at 178–185°, yielded 41.3 g. (72%) of a reddish-yellow oil soluble in 95% ethanol, methanol, chloroform, and benzene, but insoluble in 10% hydrochloric acid; n^{20}_{D} 1.5406 and d^{20}_{4} 1.1475.

Anal. Calcd. for $C_{17}H_{12}F_3N$: N, 4.88. Found: N, 4.85.

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[4] Gilman and Schulze, THIS JOURNAL, **47**, 2002 (1925).

[5] Gilman and Swiss, *ibid.*, **62**, 1847 (1940).

[6] Swarts, *J. Chim. Phys.*, **17**, 32 (1919).

DEPARTMENT OF CHEMISTRY
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RECEIVED SEPTEMBER 1, 1944

Synthesis of Stilbenecarboxylic Acids

BY GEORGE P. HAGER, A. M. VANARENDONK AND H. A. SHONLE

An investigation was undertaken to provide a satisfactory method for the preparation of certain stilbenecarboxylic acids, since methods reported in the literature are of limited applicability and are not satisfactory for the preparation of the compounds herein described.

A procedure by which 4,4′- and 2,4′-dicyanostilbenes readily can be prepared has been described.[1] It was found that these nitriles are quite resistant to acid or alkaline hydrolysis by the usual methods. The 4,4′-dicyanostilbene was readily converted into the corresponding di-imino ether hydrochloride.[2] When this was heated with water on a steam-bath, it was converted into ethyl 4,4′-stilbenedicarboxylate. This ester was readily hydrolyzed to the acid.

As previously reported,[1] 2,4′-dicyanostilbene yielded only a mono-imino ethyl ether hydrochloride, the cyano group in position 2 having failed to react. Moreover, the cyano ester, resulting on hydrolysis, could not be converted into an imino ethyl ether. The 2,4′-dicyanostilbene was hydrolyzed by acid to 2-cyano-4′-stilbenecarboxylic acid. Further hydrolysis with alkali produced the desired 2,4′-stilbenedicarboxylic acid.

Experimental Part

Diethyl 4,4′-Stilbenedicarboxylate.—4,4′-Dicyanostilbene, prepared from dibenzyl by means of bromination and treatment of the 4,4′,α,α′-tetrabromodiphenylethane with cuprous cyanide and pyridine,[1] was converted in 30-g. lots into the di-imino ethyl ether hydrochloride.[2] The imino ether hydrochloride was suspended in three times its weight of water and heated with stirring on a steam-bath for one hour or until a portion of the fluffy white solid, after washing with water, was shown to be free of nitrogen. The crude ester was filtered from the chilled reaction mixture and recrystallized from 95% alcohol or isopropyl ether. By this means a 67% yield (based on dinitrile) of colorless needles, m. p. 130–131°, was isolated.

Anal. Calcd. for $C_{20}H_{20}O_4$: C, 74.1; H, 6.2. Found: C, 74.1; H, 6.3.

The dimethyl ester, similarly prepared, was found to be far less soluble in organic solvents, and to crystallize in small plates from methyl alcohol, m. p. 227–228°. This compound was previously reported to melt at 226–227°.[3]

4,4′-Stilbenedicarboxylic Acid.—The dimethyl or diethyl ester was hydrolyzed by refluxing with 10% sodium hydroxide in ethylene glycol. In a typical run, a suspension of 12 g. of the diethyl ester in a mixture of 200 cc. of ethylene glycol, 50 cc. of water and 25 g. of sodium hydroxide, was refluxed for six hours. The reaction mixture was diluted with 2 liters of water and boiled with 10 g. of charcoal for fifteen minutes. After filtering, the free acid was precipitated with concentrated hydrochloric acid. The gelatinous precipitate was rendered filterable by heating the mixture on a steam-bath. The filtered acid was washed with water and alcohol, and dried in a desiccator over phosphoric anhydride. A 60–70% yield (based on the ester) of the dicarboxylic acid was obtained; neutral equivalent, 131. Theoretical for $C_{16}H_{12}O_4$, 134.

Anal. Calcd. for $C_{16}H_{12}O_4$: C, 71.6; H, 4.5. Found: C, 71.4; H, 4.6.

4-(ω-[2-Cyanostyryl])-benzimino Ethyl Ether Hydrochloride.—A solution of 11.5 g. of 2,4′-dicyanostilbene[1] in a mixture of 50 cc. of absolute alcohol and 125 cc. of nitrobenzene, contained in a pressure bottle, was saturated with dry hydrogen chloride at 5°. The bottle was tightly stoppered and let stand in a warm place overnight. On chilling and filtering, there was obtained 7 g. (45%) of a light yellow imino ether hydrochloride, m. p. 236–8°. From the mother liquor there was obtained by dilution with ether, 6.3 g. (40%) of a yellow solid, m. p. 223–5°. There was no significant depression in the melting points of mixtures of the two fractions.

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[1] Bance, Barber and Woolman, *J. Chem. Soc.*, 1 (1943).

[2] Ewins and Ashley, U. S. Patent 2,204,983.

[3] Meyer and Hofmann, *Monatsh.*, **38**, 358 (1917).

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.

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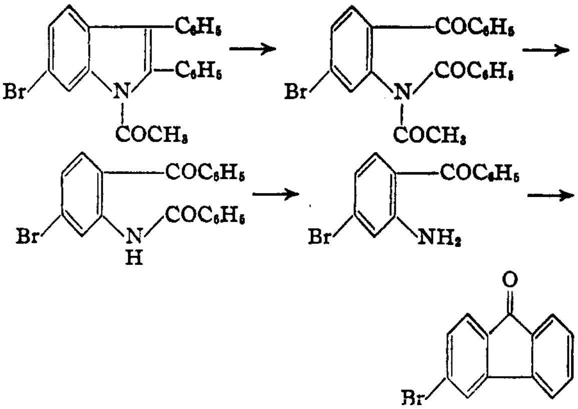
The Bromination of 1-Acetyl-2,3-diphenylindole

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.