

poured into water. The nitrile of acetylsyringic acid separated at once in the form of a colorless powder. It was purified by crystallization from hot alcohol and separated on cooling, as needles melting at 142° . The yield was 90%.

Anal. Calcd. for $C_{11}H_{11}O_4N$: N, 6.34. Found: N, 6.44, 6.22.

This acetyl compound is easily converted quantitatively into *syringic nitrile* melting at 129° by the action of dry hydrogen chloride in ether solution.

Anal. Calcd. for $C_9H_9O_4N$: N, 7.82. Found: N, 7.88, 7.80.

Syringic Aldehyde.—This aldehyde was prepared by reducing the acetylsyringic nitrile according to Stephen's method.¹² The acetyl group was removed during the reduction operation and the syringic aldehyde was produced in a yield of 70%. When allowed to crystallize slowly from a 50% alcohol solution it separated in the form of thick plates melting at 113° . The aldehyde agreed in all its properties with the description given by previous investigators, namely, Graebe and Martz, Mauthner and Pauly and Strassberger. Its semicarbazone melted at 188° .

Summary

1. A new method is described for the preparation of syringic aldehyde.
2. The nitrile of syringic acid is reduced smoothly by stannous chloride in ether solution (Stephen's method) giving this aldehyde.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

3-BENZOYLCARBAZOLE

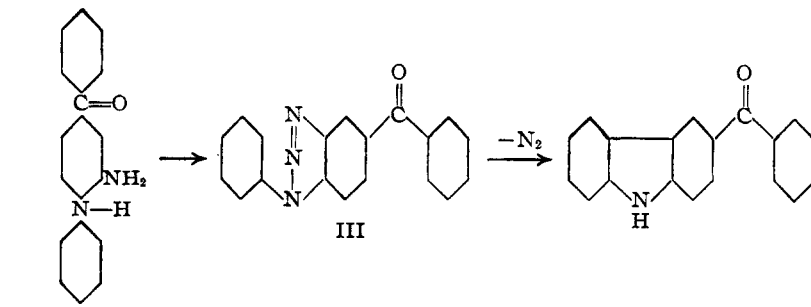
BY W. H. HUNTER AND S. F. DARLING

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As a matter of interest in a comparison of diphenylamine and carbazole, it was decided to prepare the unknown 3-benzoyl carbazole. After several attempts at shifting the benzoyl radical of the N-benzoyl derivative into the para position, the desired substance was finally obtained by making use of the carbazole synthesis of Graebe and Ullmann,¹ the benzoyl group being introduced before the ring closure.

The steps used were as follows



¹² See also Law and Johnson, *THIS JOURNAL*, **52**, 3623 (1930).

¹ Graebe and Ullmann, *Ann.*, **291**, 16 (1896).

Since the synthesis used was essentially a routine method, the 3-benzoyl-carbazole, which melted at 203–205° was characterized only by analysis, by the formation of its oxime, melting at 238°, and by the typical carbazole color reaction with concentration sulfuric acid.²

But one oxime could be obtained from the 3-benzoylcarbazole. It was therefore somewhat surprising to find that two oximes were formed simultaneously from the benzotriazole derivative, III. The low melting form, which we have called the alpha form, melts at 163–165°, and a Beckmann rearrangement showed it to be *syn*-phenyl (phenyl migrates), yielding the anilide of 1-phenyl-5-carboxybenzotriazole.

The beta form melted at 200–201°, and was shown to be *anti*-phenyl, since the Beckmann change yielded the benzoyl derivative of 1-phenyl-5-aminobenzotriazole.

For the sake of completeness, each of these rearrangement products was otherwise synthesized and compared with the original substances. Details of this are to be found in the experimental part.

Experimental Part

Preparation of *m*-Nitro-*p*-bromobenzophenone.—This substance was prepared previously by Schöpf.³ However, a much purer product in larger yields was obtained by allowing *m*-nitro-*p*-bromobenzoyl chloride to react with benzene in the presence of aluminum chloride at room temperature for twelve hours instead of on the steam-bath for three hours as described by Schöpf. By this procedure a 65% yield of an almost colorless product was obtained.

Preparation of *m*-Amino-*p*-anilide-benzophenone.—Nine and four-tenths g. of *m*-nitro-*p*-anilido-benzophenone prepared according to the method of Schöpf³ was dissolved in 150 cc. of boiling glacial acetic acid. To this hot solution was added cautiously 45 g. of stannous chloride dissolved in 100 cc. of concentrated hydrochloric acid. The solution boiled briskly. It was cooled and made alkaline with a large excess of concentrated sodium hydroxide solution. The light yellow amine which separated was filtered off and recrystallized from alcohol; yield, about 8 g. It is soluble in ethylene dibromide, hot benzene and hot alcohol, from which solvent it separates in light yellow needles. It melted at 163–165°.

Anal. Calcd. for $C_{19}H_{16}ON_2$: N, 9.72. Found: N, 9.89, 9.66.

Preparation of 1-Phenyl-5-benzoylbenzotriazole.—To the yellow reduction product suspended in glacial acetic acid was added a slight excess of sodium nitrite in solution. The amine dissolved and the yellow color disappeared. On diluting with a large amount of water, a colorless precipitate was formed which was filtered off, washed and recrystallized from dilute alcohol. The compound separates in fine silky, colorless needles which melt at 128°. The yield is almost quantitative. If hydrochloric acid is used together with the glacial acetic acid, the product develops a color which is difficult to remove.

Anal. Calcd. for $C_{19}H_{13}ON_3$: N, 14.0. Found: N, 14.3. *Mol. wt.* (ΔT ; C_6H_6). Calcd.: 299. Found: 287.

Preparation of 3-Benzoylcarbazole.—The decomposition of the 1-phenyl-5-benzoylbenzotriazole was brought about by placing it in a boat in a combustion tube and care-

² This gives a red color, changed to a dark green by a trace of nitric acid.

³ Schöpf, *Ber.*, **24**, 3771 (1891).

fully heating the boat in the furnace in an atmosphere of pure carbon dioxide. At about 328° decomposition commenced and the gas evolved was collected in an azotometer over strong potash. The gas was nitrogen. The decomposition was over at about 375°. During the decomposition a substance distilled from the boat to the cooler parts or the tube where it solidified. This was recrystallized from alcohol several times and finally melted at 203–205°. It separates in pale yellow fine crystals from alcohol. With concentrated sulfuric acid it gives a deep red coloration which turns dark green with a trace of nitric acid. The color reactions are characteristic of a carbazole derivative.

Anal. Calcd. for: $C_{15}H_{13}ON$: C, 84.1; H, 4.8; N, 5.17. Found: C, 84.4; H, 5.2; N, 5.22. *Mol. wt.* (ΔT ; C_6H_6). Calcd.: 271. Found: 309.

Preparation of the Oxime of 3-Benzoylcarbazole.—One gram of 3-benzoylcarbazole was dissolved in 50 cc. of alcohol. To this solution was added 1 g. of hydroxylamine hydrochloride and 1 g. of sodium carbonate each dissolved in 1 cc. of water. This solution was refluxed for four hours. After cooling and diluting with water a precipitate was formed which was crystallized from alcohol. It separates in small colorless prisms which melt at about 238°.

Anal. Calcd. for $C_{15}H_{13}ON_2$: N, 9.75. Found: N, 9.42.

Preparation of the α - and β -Oximes of 1-Phenyl-5-benzoylbenzotriazole.—These two compounds were made in the following manner. To a hot solution of 4 g. of 1-phenyl-5-benzoylbenzotriazole in 100 cc. of alcohol contained in a 500-cc. Erlenmeyer flask, was added 4 g. of hydroxylamine hydrochloride dissolved in 4 g. of water. The flask was connected to a reflux condenser and a solution of 4 g. of sodium carbonate in 4 g. of water was slowly added. The solution was refluxed for eight hours, after which it was diluted and the precipitate filtered and washed. Two substances were formed in about equal amount. These were best separated by heating with 50% alcohol, in which the α -oxime is very soluble. On cooling the filtered solution colorless plates of the α -oxime separated which melted at 163–165°. The β -oxime separates from 95% alcohol in almost colorless needles which melt at 200–201°.

Anal. (α -Oxime). Calcd. for $C_{19}H_{14}ON_4$: N, 17.83. Found: N, 17.68. (β -Oxime). Found: N, 17.67.

Rearrangement of the α -Oxime of 1-Phenyl-5-benzoylbenzotriazole.—One gram of the oxime was dissolved in 125 cc. of ether. To this was added finely powdered phosphorus pentachloride until an excess remained undissolved in the bottom of the flask. The ethereal solution was decanted and shaken well with cold water to decompose the halogen compound. It was then washed and dried over anhydrous sodium carbonate. On evaporation the ether solution deposited a colorless solid which was recrystallized from a large volume of ethyl alcohol. It separates from this solvent in colorless, flat prisms which melt at 227–228°.

Anal. Calcd. for $C_{19}H_{14}ON_4$: N, 17.83. Found: N, 17.56.

Preparation of the Anilide of 1-Phenyl-5-carboxybenzotriazole.—One gram of 1-phenyl-5-carboxybenzotriazole prepared according to the method of Schöpf and others⁴ was added to 5 cc. of aniline and to this solution was added slowly 5 cc. of phosphorus oxychloride. The excess of reagents was removed by washing the product with dilute hydrochloric acid and then with dilute sodium hydroxide. It was recrystallized from a large volume of alcohol, yielding colorless flat prisms which melt at 228–230°. A mixed melting point with the rearrangement product of the α -oxime of 1-phenyl-5-benzoylbenzotriazole showed no depression.

Anal. Calcd. for $C_{19}H_{14}ON_4$: N, 17.83. Found: N, 17.31.

⁴ Schöpf, *Ber.*, **22**, 3282 (1889).

Preparation of the Rearrangement Product of the β -Oxime of 1-Phenyl-5-benzoyl-benzotriazole.—This compound was prepared in practically the same manner as the rearrangement product of the α -oxime. Two grams of the beta oxime was covered with 250 cc. of ether in a 500-cc. Erlenmeyer flask. Phosphorus pentachloride was added in small portions until the β -oxime dissolved and an excess of phosphorus pentachloride remained in the bottom of the flask. The ethereal solution was decanted and shaken well with cold water. The ethereal solution on evaporation deposited an oil which solidified to a colorless substance which had the odor of ethyl benzoate. The substance melted at 226–231° after three crystallizations from ethyl alcohol. A mixed melting point of this substance with the rearrangement product of the α -oxime showed a large depression.

Anal. Calcd. for $C_{19}H_{14}ON_4$: N, 17.83. Found: N, 17.60.

Preparation of the Benzoyl Derivative of 1-Phenyl-5-aminobenzotriazole.—By treating either the tin salt or the free amine, 1-phenyl-5-amine-benzotriazole, with benzoyl chloride the benzoyl derivative was easily formed. After several crystallizations from ethyl alcohol it melted at 230–231°. A mixed melting point with the rearrangement product of the β -oxime of 1-phenyl-5-benzoylbenzotriazole showed no depression.

Anal. Calcd.: N, 17.83. Found: N, 17.93.

In the preparation of 1-phenyl-5-aminobenzotriazole by the method of Zincke and others⁵ we had occasion to prepare the corresponding nitro derivative first reported by Nietzki,⁶ who reported a melting point of 107°. Our melting point for the pure substance was 163–165°. A further search of the literature disclosed that Zincke⁵ had also prepared this compound, had found a melting point of 167° and had attributed the wide divergence in melting point to extremely impure material that Nietzki had prepared. We are of the opinion that in all probability the melting point reported by Nietzki was a typographic error.

Summary

1. 3-Benzoylcarbazole has been prepared.
2. The *syn*- and *anti*-phenyl oximes of 1-phenyl-5-benzoyltriazole have been prepared and the structure of their rearrangement products has been established by synthesis.

MINNEAPOLIS, MINNESOTA

⁵ Zincke and co-workers, *Ann.*, **313**, 273 (1900).

⁶ Nietzki, *Ber.*, **28**, 2971 (1895).