wt., 288. Found: C, 58.14; H, 8.27; mol. wt. (cryoscopic in benzene), 287.

It was hoped that this compound would condense with cyanoacetamide to give I (n = 2) with a β-ethoxyethyl group substituted in the 5 position, but this could not be accomplished under the experimental conditions used.

Acknowledgment.—The authors are grateful for the interest taken by Dr. Randolph T. Major in this investigation and for his helpful suggestions. The microanalyses were made by Messrs. Douglass Hayman, Wilhelm Reiss, Howard Clark and Richard Boos. The molecular weight determinations were made by Dr. John Conn.

Summary

1. Diethyl β-ketoadiapate has been synthesized and identified.

2. β-(4-Pyridyl)-propionic acid has been synthesized from this ester.

RAHWAY, N. J. RECEIVED DECEMBER 15 ,1942

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DUKE UNIVERSITY]

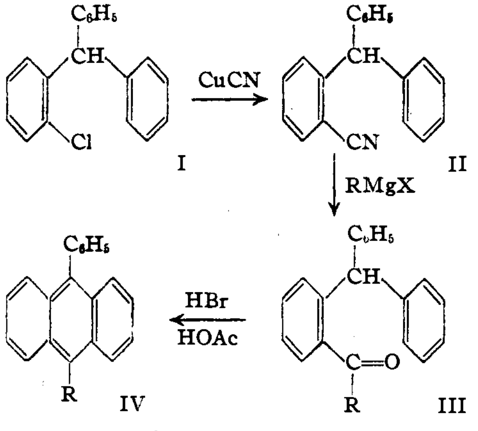
Aromatic Cyclodehydration. X.[1] 9-Alkyl- and 9-Aryl-10-phenylanthracenes

BY CHARLES K. BRADSHER[2] AND E. STUDLEY SMITH[3]

In earlier communications,[4] there has been described the cyclization of *o*-benzylphenones to give *meso* substituted hydrocarbons.

The present work was undertaken to discover whether this mode of cyclization might be extended to *o*-benzhydrylphenones. If this could be accomplished, a new method would be afforded for the synthesis of 9-alkyl- or 9-aryl-10-phenylanthracenes.

First *o*-chlorotriphenylmethane[5] (I) was converted to the nitrile[6] (II) by the action of cuprous cyanide. The nitrile (II) with phenylmagnesium bromide, on hydrolysis of the imine, gave *o*-benzhydrylbenzophenone[7] (III, R = C_6H_5). This ketone (III) when refluxed for ten days with hydrobromic and acetic acids gave 9,10-diphenylanthracene in 81% yield. If refluxing was interrupted at the end of four days, the hydrocarbon was obtained in a yield of only 45% as compared with the 75% yield of 9-phenylanthracene obtained from *o*-benzylbenzophenone under the same conditions.



In the other two cases investigated (R = CH_3 and C_2H_5), the crude ketimine was added directly to the refluxing mixture of hydrobromic and acetic acids. Apparently both hydrolysis and cyclization occurred under these conditions, for after eleven days, the expected hydrocarbons were obtained. The properties observed for our hydrocarbons are in substantial agreement with those found by previous authors.[8,9,10]

After completion of the above work, it was discovered that *o*-benzhydrylbenzophenone (III, R = C_6H_5) can be cyclized in 95% yield by heating it for only forty-five minutes in acetic anhydride containing a few drops of sulfuric acid. This method of cyclization was found to be ineffective in the case of *o*-benzylbenzophenone.

Experimental

***o*-Chlorotriphenylmethane** (I).—We found it desirable to simplify the method of Tschitschibabin[7] by eliminating the isolation of the intermediate *o*-chlorotriphenylcarbinol and by reducing with red phosphorus and iodine instead of the more expensive hydriodic acid. Thus the crude carbinol obtained from 25 g. of methyl *o*-chlorobenzoate was refluxed with acetic acid (375 cc.), water (62 cc.), red phosphorus (12.5 g.) and iodine (12.5 g.) for twenty-four

---

(1) For the preceding communications of this series see THIS JOURNAL, **63**, 493 (1941).

(2) National Research Fellow (participating basis) 1941–1942.

(3) Eastman Kodak Scholar (1941–1942).

(4) Bradsher, THIS JOURNAL, **62**, 486, 1077 (1940).

(5) Tschitschibabin, *Ber.*, **44**, 443 (1911).

(6) Drory, *ibid.*, **24**, 2563 (1891).

(7) (a) Seidel and Begner, *ibid.*, **65**, 1566 (1932); (b) Koelsch, *J. Org. Chem.*, **3**, 456 (1938).

(8) (a) Haller and Guyot, *Compt. rend.*, **138**, 1251 (1904); (b) Clar, *Ber.*, **64**, 2194 (1931).

(9) Barnett and Mathews, *ibid.*, **59**, 1429 (1926).

(10) Barnett, Cook and Wiltshire, *J. Chem. Soc.*, 1724 (1927).

hours. The product was extracted with benzene, the purified benzene extract concentrated and the residue distilled at 7 mm. pressure. The fraction boiling at 191–197°, once recrystallized from alcohol, gave 19.4 g. of white crystals, m. p. 75–77° (47.5%). A sample purified by repeated recrystallization melted at 76–77° (lit.,[5] 77°).

o-Cyanotriphenylmethane (II).—A mixture of 9.85 g. of *o*-chlorotriphenylmethane, 3.88 g. of cuprous cyanide and 15 cc. of pyridine in a sealed tube was heated at 200° for forty-eight hours. The product was then decomposed with dilute ammonium hydroxide and the organic matter extracted with benzene. The benzene solution was washed with ammonium hydroxide followed by hydrochloric acid. The product was vacuum-distilled, then crystallized from alcohol yielding 7.7 g. (81%) of the nitrile, m. p. 78–82°. A sample purified by repeated crystallization melted at 82–84° (lit.,[6] 89°) and could not be improved by further recrystallization.

o-Benzoyltriphenylmethane (III, R = C_6H_5).—The procedure was essentially that of Seidel and Begner[7a] except that the hydrolysis of the imine was considerably more difficult than indicated by the German authors. It was found that even after six hours of *refluxing* with dilute hydrochloric acid, a small quantity of the hydrochloride was obtained unchanged. The ketone formed white needles from alcohol, m. p. 82–84°, yield 60%. A sample purified by repeated recrystallization melted at 84–86° (lit., 88°[7a] and 84–86°[7b]).

9,10-Diphenylanthracene (IV, R = C_6H_5).—(a) By the action of hydrobromic and acetic acids: the *o*-benzoyltriphenylmethane (0.5 g.), acetic acid (5 cc.) and 34% hydrobromic acid (5 cc.) were refluxed together for ten days. After cooling the mixture, the crystalline diphenylanthracene was collected and recrystallized from alcohol as light yellow plates, m. p. 245–247°; yield 0.38 g. (81%). If the reaction was interupted at the end of four days, the yield was only 45% and a small quantity of unchanged ketone was recovered.

(b) By the action of acetic anhydride and sulfuric acid: to a solution of 0.61 g. of the ketone (III, R = C_6H_5) in 3 cc. of acetic anhydride, two drops of concentrated sulfuric acid was added and the solution heated on the steam-bath for forty-five minutes to complete the reaction. The mixture was allowed to cool and the diphenylanthracene collected and washed with alcohol. The product consisted of beautiful yellow crystals with an intense bluish fluorescence, m. p. 247–248° (lit., 240°[8a] and 248°[8b]); yield 0.55 g. (95%). Attempts to apply this method of cyclization to *o*-benzylbenzophenone resulted in recovery of the starting material.

9-Phenyl-10-methylanthracene[9] (IV, R = CH_3).—A Grignard reagent was prepared from 4.23 g. of methyl iodide and most of the ether distilled off. To this was added 2 g. of the nitrile in benzene (50 cc.) and the mixture was refluxed overnight. It was then decomposed with ice and ammonium chloride and the ethereal extract washed with water and sodium thiosulfate solution. The imine hydrochloride was formed by shaking the benzene solution with dilute hydrochloric acid. This precipitate was collected and refluxed for eleven days with a mixture of hydrobromic acid (20 cc.) and acetic acid (20 cc.). The product was purified by vacuum sublimation followed by crystallization from alcohol as yellow plates, m. p. 111–114°; yield 1 g. (50%). Recrystallized, it melted at 112.5–113.5° (lit.,[9] 113°).

9-Phenyl-10-ethylanthracene[10] (IV, R = C_2H_5).—This hydrocarbon was prepared in a manner analogous to that employed above. The nitrile (1.8 g.) was treated with a benzene solution of ethylmagnesium bromide and the hydrochloride of the resulting imine was treated as above. The product was crystallized from alcohol, m. p. 106–108°; yield 0.9 g. (47.5%). Recrystallized, it formed yellow plates with a blue fluorescence, m. p. 107–108.5° (lit.,[10] 110°). Despite repeated recrystallization, our melting point could not be raised further.

Anal. Calcd. for $C_{22}H_{18}$: C, 93.58; H, 6.42. Found: C, 93.70; H, 6.34.

Summary

The *o*-benzylphenone type of cyclization has now been extended to *o*-benzhydrylphenones.

DURHAM, N. C. RECEIVED NOVEMBER 20, 1942

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF PENNSYLVANIA]

Reactions of Phenanthraquinone and Retenequinone with Aldehydes and Ammonium Acetate in Acetic Acid Solution[1]

BY EDGAR A. STECK[2] AND ALLAN R. DAY

The investigations of Kreps and Day[3] and Stein and Day[4] have led to formulations of the course of reactions involved in the formation of 2-substituted oxazoles from retenequinone and phenanthraquinone or the corresponding quinonimines by reaction with aldehydes and ammonia and with aldehydes and amines. The present study represents an extension of this work to the formation of phenanthrimidazoles and retenimidazoles from phenanthraquinone and retenequinone by reaction with aldehydes and ammonium acetate in glacial acetic acid. The immediate purpose of the investigation was to determine the course of the reactions involved in imidazole formation.

---

[1] Presented at the Memphis meeting of the American Chemical Society in April, 1942.

[2] Present address, Winthrop Chemical Co., Rensselaer, N. Y.

[3] Kreps and Day, *J. Org. Chem.*, **6**, 140 (1941).

[4] Stein and Day, THIS JOURNAL, **64**, 2567, 2569 (1942).