and the precipitated dinitrotrichlorobenzene filtered, washed and recrystallized from alcohol; yields quantitative. By this procedure 1,2,3-trichlorobenzene yielded 4,5,6-trichloro-1,3-dinitrobenzene, m. p. 92–93°; 1,2,4-trichlorobenzene yielded 2,4,5-trichloro-1,3-dinitrobenzene, m. p. 102.5–103.5°; and 1,3,5-trichlorobenzene gave 2,4,6-trichloro-1,3-dinitrobenzene, m. p. 128.5°.

Reaction of the Dinitrotrichlorobenzenes with Aniline.—One gram of the dinitrotrichlorobenzene and five grams of pure aniline were heated on a water-bath for one hour. The mixture was then cooled and extracted with successive portions of 6 *N* hydrochloric acid to remove excess aniline. After filtering off the residual solid and washing with water, it was recrystallized from benzene or ethyl alcohol.

Application of this procedure to the dinitration product from 1,2,3-trichlorobenzene gave 4,6-dianilino-5-chloro-1,3-dinitrobenzene, m. p. 136–138°.

Anal. Calcd. for $C_{18}H_{13}ClN_4O_4$: N, 14.56. Found: N, 14.88, 14.91.

From the dinitration product of 1,2,4-trichlorobenzene there resulted 2,6-dianilino-5-chloro-1,3-dinitrobenzene, m. p. 182°.

Anal. Calcd. N, 14.56; Cl, 9.21. Found: N, 14.79, 14.86; Cl, 9.20, 9.28.

From the dinitration product of 1,3,5-trichlorobenzene there was obtained the previously reported 2,4,6-trianilino-1,3-dinitrobenzene, m. p. 179–180°.

Summary

1. A method for the identification of aryl halides by means of chlorosulfonylation with chlorosulfonic acid has been shown to yield excellent results.

2. Of thirty-two aryl halides studied, thirty yield characteristic arylsulfonyl chlorides readily converted to the corresponding arylsulfonamides and the other two yield reaction products characteristic of the original compound.

3. Three trichlorobenzenes have been characterized by mono-, di- and tri-nitration and the reaction products of the dinitrotrichlorobenzenes with aniline have been found useful derivatives.

CAMBRIDGE, MASS. RECEIVED AUGUST 17, 1939

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS, AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

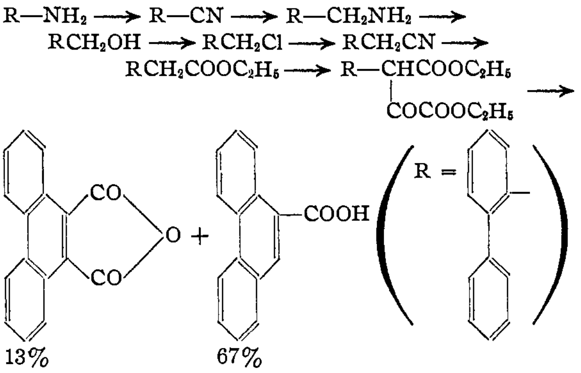
A New Synthesis of Phenanthrene Derivatives. I. Phenanthrene-9,10-dicarboxylic Anhydride and Phenanthrene-9-carboxylic Acid

BY T. A. GEISSMAN AND ROY W. TESS

In an attempt to develop a convenient method for the synthesis of phenanthrene-9,10-dicarboxylic anhydride, a modification of the Bougault method of ring closure[1] applied to the biphenyl ring system has been studied. While the results obtained are encouraging, those described in this paper are of a preliminary nature, and are published at this time because of the necessity for temporarily suspending work on the problem.

A new approach to the synthesis was sought for two reasons: the method used appeared to offer (1) a cheaper procedure and one more readily adapted to the preparation of large amounts than those of Jeanes and Adams[2] or of Weizmann, Bergmann and Berlin,[3] and (2) a synthesis which could be generalized more readily than either of those mentioned[4] to the preparation of analogous compounds containing other substituents in the rings.

The steps in the synthesis are



$$R{-}NH_2 \longrightarrow R{-}CN \longrightarrow R{-}CH_2NH_2 \longrightarrow RCH_2OH \longrightarrow RCH_2Cl \longrightarrow RCH_2CN \longrightarrow RCH_2COOC_2H_5 \longrightarrow \underset{\displaystyle COCOOC_2H_5}{R{-}CHCOOC_2H_5} \longrightarrow$$

The synthesis proceeds smoothly in the manner shown, and although suspension of the study has made it impossible to work out conditions for a quantitative ring-closure without decarboxylation, the total yield of phenanthrene derivatives is good.

The synthesis of 2-biphenylacetic acid by von Braun and Manz[5] has been accomplished by the

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[1] Bougault, *Comp. rend.*, **159**, 745 (1915); v. Auwers and Möller, *J. prakt. Chem.*, **109**, 124 (1925); Bardhan, *Nature*, **134**, 217 (1934); Fieser and Hershberg, THIS JOURNAL, **57**, 1508 (1935).

[2] Jeanes and Adams, THIS JOURNAL, **59**, 2608 (1937).

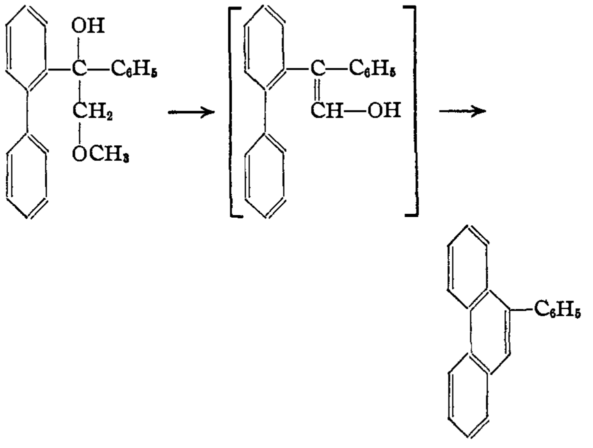
[3] Weizmann, Bergmann and Berlin, THIS JOURNAL, **60**, 1331 (1938).

[4] The synthesis of Weizmann, *et al.*[3] is based upon the preparation by Gruber and Adams [THIS JOURNAL, **57**, 2555 (1935)] of the adduct of dicyclohexenyl and maleic anhydride.

[5] Von Braun and Manz, *Ann.*, **468**, 273 (1929).

same series of reactions up to the formation of 2-biphenylacetonitrile. The step involving the reduction of the nitrile to the methylamine has been improved in the present work with the elimination of the side-reaction leading to unwanted secondary amine.

The suggestion of Bradsher[6] that ring closure of compounds such as 1-phenyl-1-(2-biphenyl)-2-methoxyethanol-1 proceeds through an intermediate carbonyl compound (or its enol form)



finds support in the present work. The alkali-solubility and violet color with ferric chloride shown by ethyl 2-biphenyloxalylacetate indicate that it exists completely as the enol and lead to the belief that 2-biphenylacetaldehydes or acetones are cyclized through their respective enols.

Experimental

The synthesis of 2-biphenylacetonitrile is described by von Braun and Manz[5] but since numerous details are lacking in this article, a more detailed description of several of the steps involved seems desirable.

o-Phenylbenzylamine.—A mixture of 122.5 g. of o-cyanobiphenyl (distilled from Raney nickel), one teaspoonful of Raney nickel, 150 cc. of liquid ammonia and 50 cc. of ether was placed in a bomb under a pressure of 3350 lb. (223 atm.) of hydrogen. Upon heating to 120° the pressure rose to 4500 lb. (300 atm.), then gradually fell to 1670 lb. (111 atm.) in about four hours. After the bomb was cooled and the pressure released, the ammonia was allowed to evaporate and the residue dissolved in ether and filtered. The filtrate was extracted with dilute hydrochloric acid and the product recovered by ether extraction of the neutralized solution and distilled. The product boiled almost entirely at 163–168° (15 mm.) and practically no higher-boiling residue remained in the distillation flask (von Braun and Manz[5] give b. p. 163° (12 mm.)).

o-Phenylbenzyl Alcohol.—A solution of 17.9 g. of sodium nitrite in 25 cc. of water was added over ten minutes to a cooled solution of 12.0 g. of o-phenylbenzylamine in 50 cc. of acetic acid. When all the nitrite had been added the solution was stirred for ten minutes at room temperature and poured into water. The solution was neutralized with solid sodium carbonate and extracted with ether. Unchanged amine was removed by washing the ether solution with dilute acid and after removal of the ether the product was distilled. The fraction boiling at 177–184° (15 mm.) weighed 11.5 g. (v. Braun and Manz[5] give b. p. 174° (13 mm.)).

o-Phenylbenzyl Chloride and o-Phenylbenzyl Cyanide.—These were prepared by methods too well known to require detailed description. The chloride boiled at 161–168° (16 mm.) (v. Braun and Manz[5] give 154° (12 mm.)). The cyanide boiled at 181–190° (15–16 mm.) (v. Braun and Manz[5] give 182° (12 mm.)).

Ethyl 2-Biphenylacetate.—To a solution of 55 g. of 95% alcohol and 45 g. of concentrated sulfuric acid was added 43.3 g. of 2-biphenylacetonitrile. The solution was gently refluxed for thirteen hours and poured into water. The ester was extracted with ether and distilled. There was obtained 55.2 g. of ester, b. p. 180–185° (15 mm.). The identity of the ester was established by saponifying a sample of it to the known[5] 2-biphenylacetic acid.

Phenanthrene-9,10-dicarboxylic Anhydride and Phenanthrene-9-carboxylic Acid.—The oxalylation of ethyl 2-biphenylacetate by means of dry potassium ethoxide was found to be superior to the method in which metallic sodium is used; the latter method was found to give good results when applied to the oxalylation of ethyl phenylacetate by Rising and Stieglitz.[7]

Potassium ethoxide was prepared by allowing 2.0 g. of powdered potassium covered with 50 cc. of dry ether to react with 2.5 g. of absolute ethanol. To the ice-cooled suspension of the resulting potassium salt was added a mixture of 7.5 g. of ethyl oxalate and 12.0 g. of ethyl 2-biphenylacetate. The potassium ethoxide dissolved and a greenish-brown solution resulted, which in the course of two days turned a yellow-red in color. The solution was decomposed with cracked ice and the aqueous layer separated. The ether layer was washed well with small portions of ice water and the combined aqueous extracts acidified with ice-cold, dilute sulfuric acid. The product was extracted with ether, the ether solution dried and evaporated. The oxalyl derivative was obtained as a pale yellow oil which gave a deep violet coloration with alcoholic ferric chloride. Attempts to crystallize it were fruitless; it showed a tendency to decompose upon prolonged exposure to air.

To the oily oxalyl ester was added a mixture of 50 cc. of glacial acetic acid and 30 cc. of 48% hydrobromic acid and the mixture refluxed for three hours. After fifteen to twenty minutes of refluxing, yellow needles began to form and a heavy precipitate soon filled the solution. The mixture was cooled and the product collected. It was pale yellow, crystalline and weighed 7.95 g.

The ether layer containing the non-acidic material from the oxalylation reaction yielded 2.7 g. of unchanged ethyl 2-biphenylacetate.

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(6) Bradsher, THIS JOURNAL, **61**, 3131 (1939).

(7) Rising and Stieglitz, THIS JOURNAL, **40**, 723 (1918).

The crude material melted poorly and proved to be a mixture. Recrystallized from acetic anhydride, it yielded 1.25 g. of yellow needles of the anhydride melting at 310–315° (literature, 312°[3] and 322°[2]), and 6.0 g. of colorless needles of the acid, melting at 249–250° (literature[8] 250°). The acid was converted to methyl phenanthrene-9-carboxylate, white needles from methanol, m. p. 115–116° (literature[9] 116°).

Summary

1. The synthesis of phenanthrene-9,10-dicarboxylic anhydride and phenanthrene-9-carboxylic acid by ring closure of ethyl 2-biphenyloxalylacetate is described.

2. The method described constitutes a new synthesis of phenanthrene derivatives.

URBANA, ILLINOIS RECEIVED DECEMBER 26, 1939
LOS ANGELES, CALIFORNIA

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[8] Werner and Kunz, *Ann.*, **321**, 327 (1902).

[9] Mosettig and van de Kamp, THIS JOURNAL, **52**, 3704 (1930).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Sterols. LXXXVII. Cholesterol and Sitosterol Derivatives

BY RUSSELL E. MARKER AND EWALD ROHRMANN

Inasmuch as most of the oxidation studies on the sterols have been made with chromic anhydride in acetic acid, it seemed of interest to study the action of potassium permanganate in acetic acid on some of these substances. It is well known that potassium permanganate in alkaline medium oxidizes cholesterol to a cholestanetriol-3,5,6,[1,2,3] the reagent under these conditions apparently having no tendency to oxidize the secondary alcohols to ketones. The resulting triol differs from that obtained by the hydroxylation of cholesterol with hydrogen peroxide. That this difference is due to the configuration of the tertiary hydroxyl group at C-5 is indicated by the fact that the two triols on oxidation with chromic anhydride yield different cholestanol-5-diones-3,6.

In acetic acid solution cholesterol with potassium permanganate yields a cholestanol-5-dione-3,6 which is very probably identical with that obtained by oxidizing with chromic anhydride the alkaline permanganate oxidation product of cholesterol. With cholesteryl acetate a 3-acetoxy-5-hydroxy-6-ketocholestane was obtained. Similar results were obtained with sitosterol and sitosteryl acetate. The same products were obtained when the oxidations were conducted at room temperature or at 55°, there apparently being little tendency for ring B to open between C-5 and C-6.

The oxidation of cholestanol-3(β) with potassium permanganate in acetic acid solution at room temperature gave a good yield of cholestanone. At a temperature of 55° both cholestanone and 2,3-cholestane dicarboxylic acid were obtained. The oxidation of neocholestene at room temperature gave largely 2,3-cholestane dicarboxylic acid.

The preparation of 7-ketositosteryl chloride has been carried out by the chromic anhydride oxidation of sitosteryl chloride.[4] The substance undergoes reactions analogous to those of 7-ketocholesteryl chlorides.[4,5]

We wish to thank Parke, Davis and Company for their generous help and assistance during the various phases of this work.

Experimental Part

Oxidation of Cholesterol and Sitosterol Derivatives with Potassium Permanganate.—(a) **Cholesterol.**—To a solution of 2 g. of cholesterol in 150 cc. of acetic acid was added 75 cc. of 1 *N* aqueous potassium permanganate and 75 cc. of acetic acid. After standing for six hours at room temperature the mixture was diluted with water and the solid taken up with ether. The ethereal extract was washed with water and dilute sodium carbonate solution and the ether evaporated to yield approximately 1.6 g. of crystalline residue. This was crystallized from acetone to give compact white crystals, m. p. 248–251°.

Anal. Calcd. for $C_{27}H_{44}O_3$: C, 77.8; H, 10.65. Found: C, 78.0; H, 10.7.

(b) **Cholesteryl Acetate.**—To a solution of 2 g. of cholesteryl acetate in 210 cc. of acetic acid heated at 45–50° was added 50 cc. of 1 *N* aqueous potassium permanganate over a period of thirty minutes and the mixture was heated at 50° for an additional thirty minutes. The product was worked up and crystallized from acetone as described above to give white plates, m. p. 231–233°.

Anal. Calcd. for $C_{29}H_{48}O_4$: C, 75.6; H, 10.5. Found: C, 75.8; H, 10.7.

Similar results were obtained when the oxidation was conducted at room temperature.

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[1] Windaus, *Ber.*, **40**, 257 (1907).

[2] Pickard and Yates, *J. Chem. Soc.*, **93**, 1678 (1908).

[3] Pimone, *Gazz. chim. ital.*, **62**, 1101 (1932).

[4] Marker, *et al.*, THIS JOURNAL, **59**, 619 (1937).

[5] Marker and Rohrmann, *ibid.*, **61**, 3022 (1939).