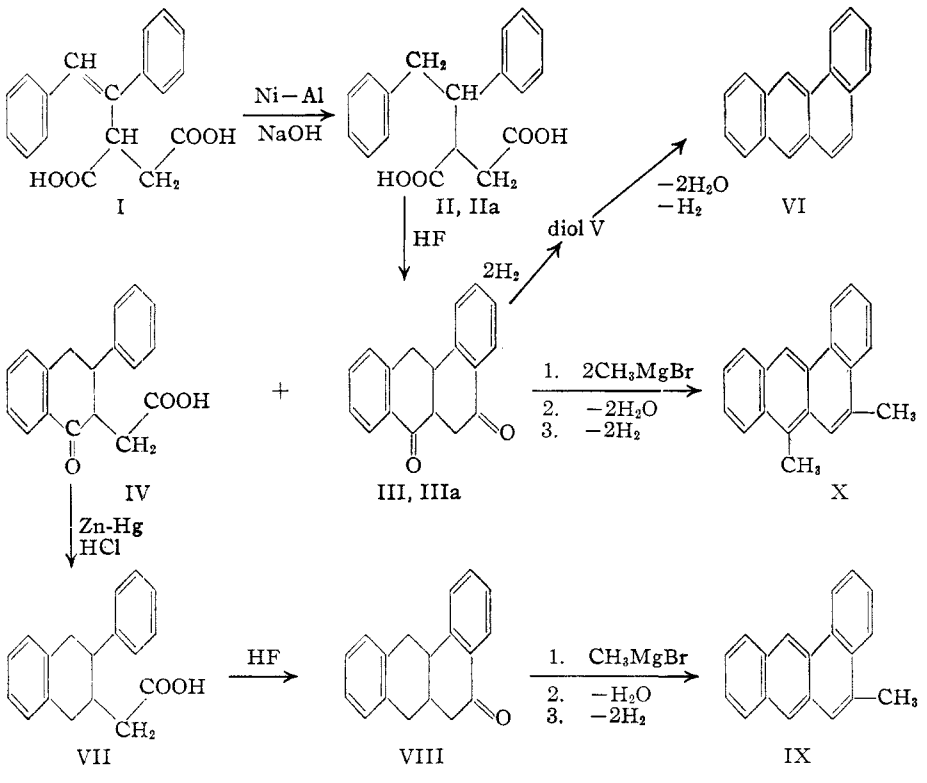
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY]

A New Synthesis of 1,2-Benzanthracene[1]

BY MELVIN S. NEWMAN AND ROBERT T. HART

Since known syntheses for the 1,2-benzanthracene nucleus appeared inadequate for the synthesis of 1,9-dimethyl-1,2-benzanthracene[2,3] we have developed a new method[4] and have applied it to the syntheses of 1,2-benzanthracene, VI, 3-methyl-1,2-benzanthracene, IX, and 3,10-dimethyl-1,2-benzanthracene, X. The steps are outlined in the chart.[5]



The unsaturated acid, I, obtained by a modified Stobbe condensation from desoxybenzoin and methyl succinate,[6] was reduced to a mixture of stereoisomeric saturated acids, II and IIa, in high yield using Raney nickel and alkali.[7] The double ring closure of the saturated acid mixture afforded the diketones, III and IIIa, in only 27% yield, the major (48%) product being a keto acid,[8] IV, whose structure was proved by conversion as shown to the known 3-methyl-1,2-benzanthracene.[9] The keto acid could also be cyclized in fair yield to the diketones, III, IIIa, with hydrogen fluoride.

The conversion of the diketones, III and IIIa, into VI and X offered no difficulties. The hydrocarbons, VI, IX, and X were further characterized by the formation of their addition complexes with 2,4,7-trinitrofluorenone.[10] These complexes are formed with great ease and in our opinion are superior to the similar complexes with picric acid or *s*-trinitrobenzene for identification purposes.

Disregarding stereochemical isomerism, the saturated acids, II and IIa, may be considered as disubstituted γ-phenylbutyric acids, one of which carries an α-(CH_2COOH) and a β-(C_6H_5) group, and the other a β-(COOH) and a γ-($C_6H_5CH_2$) group. It is interesting that the acid cyclizes preferentially as an α,β-disubstituted γ-phenylbutyric acid rather than as the β,γ-analog.

Work on the adaptation of this synthesis to the preparation of 1′,9-dimethyl-1,2-benzanthracene is in progress in this Laboratory.

Experimental[11]

(1,2-Diphenylvinyl)-succinic Acid, I.—A hot solution of 73 g. (0.37 mole) of desoxybenzoin in 54 g. (0.37 mole) of dimethyl succinate was added over a period of thirty minutes to 40 g. (0.74 mole) of hot dry sodium methoxide in a round-bottomed flask swept with dry nitrogen and fitted with a stirrer and reflux condenser. The methanol which was formed in the spontaneous strongly exothermic

(1) The material herein presented is taken from the Ph.D. thesis of Robert T. Hart presented to the Graduate School of The Ohio State University, August, 1946. Present address: Standard Oil Company of California, Richmond, Calif.

(2) Fieser and Seligman, THIS JOURNAL, **60**, 170 (1938).

(3) Newman, *ibid.*, **62**, 2295 (1940).

(4) The authors wish to express their gratitude to Dr. W. S. Johnson, University of Wisconsin, who had independently started work along similar lines, for deferring to our interests in this problem.

(5) Hewett, *J. Chem. Soc.*, 585 (1942), published a brief account of the beginning steps of this synthesis which appeared after our experiments were well along. Our work was also interrupted by the war.

(6) Stobbe and Russwarm, *Ann.*, **308**, 157 (1899).

(7) Schwenk, Papa, Whitman and Ginsberg, *J. Org. Chem.*, **9**, 2, 175 (1944).

(8) This acid is undoubtedly that obtained previously by Borsche and Sinn, *Ann.*, **555**, 70 (1943), who reported a melting point of 170–171° but did not prove its structure.

(9) (a) Cook, *J. Chem. Soc.*, 1087 (1930); (b) Cook and Robinson, *ibid.*, 505 (1938).

(10) Orchin and Woolfolk, THIS JOURNAL, **68**, 1727 (1946)

(11) All melting points corrected.

reaction was allowed to distill during the addition of the reagents and also during an additional heating period of thirty minutes. After cooling to room temperature during two hours the reaction mixture which formed a brown cake was saponified with 10% sodium hydroxide. The neutral fraction was extracted with benzene and the acid fraction, after recrystallization from benzene, yielded 68 g. (60%) of pure I,[5] m. p. 151.2–152.0°.

α-(1,2-Diphenylethyl)-succinic Acid, II, IIa.—To a solution maintained at 90° of 10 g. of I in 300 cc. of 10% sodium hydroxide was added 30 g. of Raney nickel alloy over a period of eight hours. The mixture of saturated acids, II and IIa, thus produced was separated by fractional recrystallization from alcohol whereby 3.6 g. of the higher melting isomer II, was obtained as colorless crystals, m. p. 189.0–189.5°. After replacement of the alcohol by benzene, 4.4 g. of the lower melting isomer, IIa, m. p. 137.2–138.0°, was obtained. These melting points correspond to those reported by Hewett.[5]

3,10-Diketo-3,4,4a,9,9a,10-hexahydro-1,2-benzanthracene, III, IIIa.—A solution of 30 g. of a mixture of II and IIa in 600 g. of anhydrous hydrogen fluoride in a copper container was allowed to stand a day, after which the residue was poured on ice and separated into acid and neutral fractions. Fractional recrystallization of the neutral fraction, 7.1 g., 27%, from alcohol and then aqueous alcohol afforded 2.7 g. (10%) of long prisms of the higher melting form, m. p. 211–212°, of diketone, III, and 2.9 g. (11%) of rosets of fine needles of the lower melting form, m. p. 132.0–132.5°. These melting points correspond to those reported by Hewett.[5] Approximately the same mixture of diketones was obtained when either pure acid, II or IIa, was used. The above cyclization was considerably better than that using sulfuric acid or that employing the acid chloride and aluminum chloride.

3,10-Dihydroxy-3,4,4a,9,9a,10-hexahydro-1,2-benzanthracene, V.—Application of the Meerwein–Ponndorf reduction to 2 g. of the high melting diketone, III, afforded 1.76 g. (87%) of colorless fine needles of V, m. p. 184–185°. Recrystallization from benzene raised the melting point to 185.5–186°.

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.3; H, 6.8. Found: C, 81.3; H, 6.9.

1,2-Benzanthracene, VI.—Aromatization of 700 mg. of V was effected by heating with 69 mg. of a 5% palladium-on-charcoal catalyst[12] at 270° for twenty minutes and at 320° for forty-five minutes. The crude hydrocarbon was obtained in 85% yield by crystallization from alcohol. Vacuum sublimation, followed by crystallization from alcohol, afforded 365 mg. (61%) of colorless 1,2-benzanthracene, m. p. 159.5–160.0°. Its identity was established by conversion to the orange *s*-trinitrobenzene addition complex, m. p. and mixed m. p. 159.8–160.2°. The trinitrofluorenone[10] derivative formed minute rose colored crystals, m. p. 221.0–221.6°, on mixing equimolar solutions of the two components in hot alcohol.

Anal. Calcd. for $C_{31}H_{17}O_7N_3$: C, 58.5; H, 3.2; N, 7.7. Found: C, 58.4; H, 3.5; N, 7.9.

3,10-Dimethyl-1,2-benzanthracene, IX.—A solution of 1.5 g. of the higher melting diketone, IIIa, in dry benzene was refluxed with a large excess of methylmagnesium bromide, after which the mixture was treated with ammonium chloride solution. The organic material was isolated by ether extraction and heated from 260 to 320° during ninety minutes with 100 mg. of palladium-on-charcoal catalyst to effect dehydration and dehydrogenation. A filtered benzene solution of this product was chromatographed on an alumina column and the eluted material recrystallized from petroleum ether (Skellysolve C) to yield 810 mg. (54%) of shining colorless plates of 3,10-dimethyl-1,2-benzanthracene, IX, m. p. 143.6–143.8°. The picrate, which crystallized in maroon needles, melted at 181.8–182.2° and the trinitrofluorenone[10] derivative, brownish purple micro crystals, melted at 250–251°.

Anal. Calcd. for $C_{20}H_{16}$: C, 93.8; H, 6.2. Found: C, 93.5; H, 6.4. Calcd. for $C_{26}H_{19}N_3O_7$: C, 64.4; H, 4.0; N, 8.7. Found: C, 64.0; H, 4.5; N, 9.0. Calcd. for $C_{33}H_{21}N_3O_7$: C, 68.4; H, 3.7; N, 7.3. Found: C, 68.4; H, 4.2; N, 7.0.

(1,2,3,4-Tetrahydro-1-keto-3-phenyl-2-naphthyl)-acetic Acid, IV.—The acid fraction obtained from the above cyclization of the acid mixture, II and IIa, yielded 18.0 g. (64%) of a brown solid. On decolorization with charcoal and crystallization from benzene there was obtained 13.5 g. (48%) of keto acid, IV, m. p. 169–171°. An analytical sample, twice crystallized from benzene, melted at 173.8–174.2°.[8]

Anal. Calcd. for $C_{18}H_{16}O_3$: C, 76.9; H, 5.8; neut. equiv., 280. Found: C, 77.0; H, 5.6; neut. equiv., 284.

When a solution of 1.5 g. of IV in 57 g. of hydrogen fluoride was allowed to stand for twenty-four hours, and the reaction mixture was worked up in the usual manner, 0.25 g. of diketone, III, m. p. 211–212° and 0.19 g. of diketone, IIIa, m. p. 132.0–132.5°, were obtained.

Lactone of 1-Hydroxy-3-phenyl-1,2,3,4-tetrahydro-2-naphthylacetic Acid.—Attempted reduction of the keto group of IV to a methylene group with Raney nickel and alkali, as in the preparation of II and IIa, yielded instead the lactone formed by cyclization of the intermediate hydroxy-acid. It was formed in 80% yield and melted at 171.8–172.6°. A mixed melting point with IV was depressed 36°.

Anal. Calcd. for $C_{18}H_{16}O_2$: C, 81.8; H, 6.1. Found: C, 81.3; H, 6.2.

(1,2,3,4-Tetrahydro-3-phenyl-2-naphthyl)-acetic Acid, VII.—A mixture of 10 g. of IV, 25 g. of amalgamated zinc, 40 cc. of toluene,[13] 35 cc. of concentrated hydrochloric acid, and 15 cc. of water was refluxed for thirty hours with four 8-cc. additions of hydrochloric acid during the reaction. The product was taken into alkali, precipitated with acid, and recrystallized from petroleum ether (Skellysolve C) to yield 8.7 g. (86%) of VII, m. p. 114–115°. The analytical sample melted at 115.5–116.2°.

Anal. Calcd. for $C_{18}H_{18}O_2$; C, 81.2; H, 6.8; neut. equiv., 266. Found: C, 80.9; H, 6.9; neut. equiv., 261.

3-Keto-3,4,4a,9,9a,10-hexahydro-1,2-benzanthracene, VIII.—A solution of 2.5 g. of VII in 75 g. of liquid anhydrous hydrogen fluoride was allowed to stand in a copper vessel for twenty hours. The residue was treated with ice and the organic material taken into ether. No acidic fraction was recovered on extraction with carbonate. The neutral fraction afforded 2.01 g. (86%) of VIII as colorless micro crystals, m. p. 121–122°, from aqueous alcohol. The analytical sample, m. p. 122.8–123.6°, was obtained by crystallization from Skellysolve C.

Anal. Calcd. for $C_{18}H_{16}O$: C, 87.1; H, 6.5. Found: C, 86.9; H, 6.4.

3-Methyl-1,2-benzanthracene, IX.—A solution of 700 mg. of VIII in benzene was added to 15 cc. of 1.14 *N* methylmagnesium bromide. After refluxing for one hour, the product was isolated as usual. Dehydration and dehydrogenation was effected by heating at 270–310° for one hour over 70 mg. of palladium-on-charcoal catalyst. Purification by vacuum sublimation and crystallization from Skellysolve C afforded 421 mg. (61.6%) of slightly yellow crystals, m. p. 151–152°. Two crystallizations from Skellysolve C yielded a colorless product, m. p. 154.2–155°. Purification of the crude product was easier if chromatography over alumina was used. The picrate melted at 152.4–153.0°. Cook[9b] gives melting points of 155 and 153°, respectively, for these compounds.

Summary

A new general method of synthesis of 1,2-benz-

(12) Gatterman and Wieland, "Laboratory Methods of Organic Chemistry," 24th ed., The Macmillan Co., New York, N. Y., 1941, p. 278.

(13) Martin, THIS JOURNAL, **58**, 1438 (1936).

anthracene and its mono- and dialkyl derivatives is described.

Desoxybenzoin was condensed with dimethyl succinate to yield α-(1,2-diphenylvinyl)-succinic acid, I, which was reduced to two stereoisomeric saturated acids, α-(1,2-diphenylethyl)-succinic acids, II and IIa. The mixture of acids was cyclized with liquid, anhydrous hydrogen fluoride to form two stereoisomeric diketones, III and IIIa, and a keto acid, IV.

The diketone was reduced to a diol, V, which was dehydrated and dehydrogenated to 1,2-benzanthracene, VI. The diketone was also converted to 3,10-dimethyl-1,2-benzanthracene, X, by reaction with methylmagnesium bromide followed by dehydration and dehydrogenation.

The keto acid was identified as (1,2,3,4-tetrahydro-1-oxo-3-phenyl-2-naphthyl)-acetic acid, by its conversion to the known 3-methyl-1,2-benzanthracene, IX, in the following synthetic steps: Clemmensen reduction to (1,2,3,4-tetrahydro-3-phenyl-2-naphthyl)-acetic acid, VII, cyclization with hydrogen fluoride to 3-keto-3,4,4a,9,9a,10-hexahydro-1,2-benzanthracene, VIII; and reaction with methylmagnesium bromide followed by dehydration and dehydrogenation to 3-methyl-1,2-benzanthracene, IX.

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Isomeric Chlorinated Long-Chain Esters

BY HERBERT H. GUEST

In a recent paper from this Laboratory[1] it was shown that certain long-chain methyl esters react with chlorine to form mixtures and that attempts to find a method of determining the position of the substituent chlorine, using alkaline reagents, were unsuccessful.

The results now reported were obtained by the use of sodium acetate in acetic acid solution. This reagent, acting on the monochloro ester fraction, gave products which could be quantitatively differentiated. The more difficult problem of the structure of the dichloro esters is not considered in this paper.

Preliminary work involved the preparation of monochloro esters in which the position of the chlorine was definitely known and the study of their reaction with sodium acetate. Thus it was found that α-chloro esters formed exclusively acetoxy esters, β-chloro esters formed only α,β-unsaturated esters and γ- or Δ-chloro esters formed acetoxy esters which were readily hydrolyzed to the corresponding lactones.[2]

Trial of the methods described in the literature for preparing α-chloro acids led to the conclusion that the most suitable was that used by Staudinger and co-workers[3] to prepare α-chlorobutyric acid.

The beta isomer was prepared by the Perkin–Knoevenagel reaction, as modified by Zaar[4] followed by the addition of hydrogen chloride.

This addition took place only when the double bond was in the alpha–beta position. It was found that oleic and undecylenic acids, for example, were not acted on by hydrogen chloride under similar conditions. On the other hand, the usual iodine absorption methods gave erratic results with α,β-unsaturated esters.[5] In order to estimate the latter, it was found necessary to use bromine.

The method of Noyes and Cox[6] gives excellent yields of γ-chloro esters from the corresponding γ-lactones. A representative of the Δ-chlorinated series was obtained by hydrolysis and esterification of 4-chlorovaleronitrile.[7]

For an extended study of the products of direct chlorination, hexoyl chloride was chosen as the starting material. After chlorination, the reaction mixture was esterified with methanol. The monochloro ester fraction, obtained by careful distillation *in vacuo*, was caused to react with fused sodium acetate in glacial acetic acid solution. This procedure was also followed in the study of the products obtained by chlorinating methyl hexoate, octoate and stearate. The products obtained by chlorinating either the acid chloride or the methyl ester were almost identical.

Experimental

Preparation of α-Chloro Acids.—Alkyl malonic acids were obtained by following the directions given in "Organic Syntheses."[8] Butyl, hexyl, heptyl, dodecyl and hexadecylmalonic acids thus prepared, were chlorinated in boiling ethereal solution by the gradual addition of one mole of sulfuryl chloride. The reaction mixture was refluxed for three hours and was then washed with cold water. The latter operation requires care since the chloro acids are water-soluble.

Upon heating at 130–140° for thirty minutes, the chloro-

(1) H. H. Guest and C. M. Goddard, Jr., THIS JOURNAL, **66**, 2074 (1944).

(2) L. Henry, *Z. physik. Chem.*, **10**, 111 (1892); H. S. Taylor and H. W. Close, THIS JOURNAL, **39**, 422 (1917).

(3) H. Staudinger, E. Anthers and H. Schneider, *Ber.*, **46**, 3539 (1913); *cf.* A. M. Clover, *Ann.*, **319**, 357 (1902).

(4) B. Zaar, *Ber., Schimmel & Co.*, 299 (1929); "Organic Reactions," Vol. I, John Wiley & Sons, New York, N. Y., 1942, p. 252; *cf.* A. M. Clover, ref. 3.

(5) *Cf.* G. Ponzio and C. Gastaldi, *Gazz. chim. ital.*, **42**, 92 (1912).

(6) W. A. Noyes and I. J. Cox, THIS JOURNAL, **25**, 1094 (1903).

(7) German Patent 120,138 (*Chem. Centr.*, **72**, I, 1126 (1901); I. K. Phelps and E. W. Tillotson, Jr., *Am. J. Sci.*, [4] **26**, 264 (1908).

(8) "Organic Syntheses," Coll. Vol. I, p. 245; A. W. Dox, THIS JOURNAL, **46**, 1707 (1924).