[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

Polynuclear Aromatic Hydrocarbons. II.[1] Friedel–Crafts Condensations with 9,10-Dihydrophenanthrene

BY DONALD D. PHILLIPS AND EARL J. MCWHORTER[2]

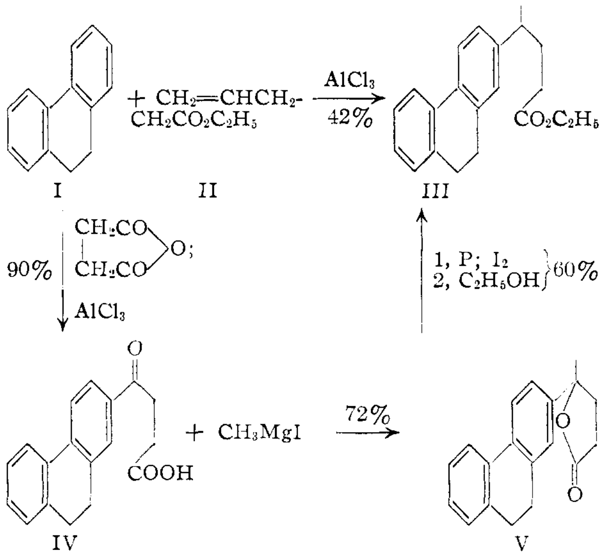
RECEIVED MARCH 26, 1954

The Friedel–Crafts reactions of 9,10-dihydrophenanthrene have been extended to include unsaturated esters and lactones so that convenient syntheses of branched-chain esters (*cf.* III) are now available. That carbon 2 is the point of attack in these reactions has been demonstrated in one instance by an unequivocal synthesis and in another by conversion of the product to the Diels hydrocarbon (IX).

It has recently been shown[1] that 9,10-dihydrophenanthrene (I) is a suitable precursor for the preparation of the pentacyclic hydrocarbon, picene. In order to extend this model synthesis to the substituted picenes, especially those obtained from triterpene dehydrogenations, we have investigated various methods of preparing compounds corresponding to the general structure of III. Further condensations of III with suitably constituted anhydrides or acid chlorides should occur at carbon 7[1] thus giving rise to compounds with the necessary structural features for closure to picene derivatives.

A standard preparative method for substituted valeric esters (*cf.* III) in the polynuclear aromatic series involves a Friedel–Crafts condensation of succinic anhydride followed by conversion of the resultant ketoacid to a lactone which is subsequently opened and then esterified (*cf.* I → IV → V → III, Chart I).[3]

CHART I



Since yields by this rather circuitous route are often poor, we have investigated the Friedel–Crafts condensation of unsaturated esters and lactones whereby compounds similar to III should be obtained directly.[4] However, when 9,10-dihydrophenanthrene (I) and ethyl allylacetate (II) were subjected to the Friedel–Crafts condensation in the presence of nitrobenzene solvent, the product was a mixture of III and the fully aromatized phenanthrene derivative. The peak at 252 mμ (log ϵ 4.43) in the ultraviolet absorption spectrum indicated the presence of almost 30% of the latter compound. In addition, unreacted dihydrophenanthrene (I) was always recovered from the reaction mixture contaminated with phenanthrene, even when carefully recrystallized (I) was used as starting material. It was suspected that these side reactions were a result of oxidation by the nitrobenzene, and to substantiate this postulate the reaction was carried out in the presence of ethylene chloride as solvent. The product under these conditions showed the broad band at 267 mμ characteristic of dihydrophenanthrene derivatives[5] and the absence of a peak at 252 mμ indicated that the compound was essentially free of phenanthrene contaminant. Similarly, the condensation between I and γ-valerolactone gave large amounts of oxidized product when carried out in nitrobenzene solvent whereas a 32% yield (after esterification) of ester III could be obtained when the solvent was ethylene chloride.

Although previous work has shown that Friedel–Crafts condensations between 9,10-dihydrophenanthrene and acid chlorides or anhydrides give principally the 2-substituted compound,[6] we considered it advisable to establish unequivocally the structure of III so that the generalization could be extended to lactones and unsaturated esters. This was accomplished by the succinoylation of 9,10-dihydrophenanthrene to give the known acid IV[1,6] followed by conversion to the lactone V which was opened and the resultant acid esterified to give III. When this compound was compared to the ester prepared by the direct condensation of either allylacetic ester or γ-valerolactone, the two were found to be identical.

Further substantiation for this assignment came from a study of the ester VI obtained from the reaction between ethyl vinylacetate and 9,10-dihydrophenanthrene (I). To establish the location of the side chain in this compound it was dehydrogenated, saponified and the resultant acid cyclized to the ketone VIII. The modified Wolff–Kishner reduction smoothly converted this ketone to the Diels hydrocarbon IX, thus proving the structure of the initial ester VI and at the same time providing a convenient synthesis of this hydrocarbon.

---

(1) Paper I, D. D. Phillips, THIS JOURNAL, **75**, 3223 (1953).

(2) Shell Fellow in Chemistry, 1953–1954.

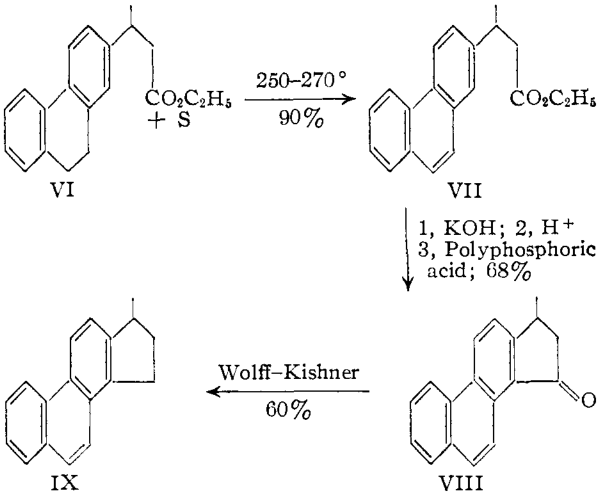
(3) L. F. Fieser and W. S. Johnson, THIS JOURNAL, **61**, 1647 (1939).

(4) (a) S. M. Mukherji and N. K. Bhattacharyya, *J. Org. Chem.*, **17**, 1202 (1952); **18**, 1499 (1953); (b) J. Colonge and R. Domenech, *Bull. soc. chim. France*, 634 (1952); (c) W. L. Mosby, THIS JOURNAL, **74**, 2564 (1952); *J. Org. Chem.*, **18**, 964 (1953).

(5) R. N. Jones, THIS JOURNAL, **63**, 1658 (1941).

(6) A. Burger and E. Mosettig, *ibid.*, **59**, 1302 (1937).

CHART II



The yields obtained in these condensations are rather low (32–42%) when compared to the succinoylation (I → IV) which is almost quantitative. This is probably because of the strong *meta*-directing influence of the ketoacid side chain which makes the introduction of a second group in IV essentially impossible,[1] whereas esters III and VI are more reactive toward further substitution than is dihydrophenanthrene itself. This interpretation is consistent with the fact that the high-boiling residues contain considerable dialkylated product even though some dihydrophenanthrene is always recovered from the reaction unchanged. In spite of these lower yields the one-step conversions are naturally less time-consuming and hence represent a superior synthetic method. Since ethyl allylacetate is difficult to prepare and γ-valerolactone is commercially available, the reaction involving the lactone becomes the method of choice.

Experimental[7]

Starting Materials.—9,10-Dihydrophenanthrene was prepared as previously reported.[1] γ-Valerolactone and ethylene chloride were Eastman Kodak Co. practical grade reagents, freshly distilled before use. Ethyl vinylacetate, b.p. 121–123°, n^{21}_D 1.4112, was prepared from vinylacetic acid[8] in the normal manner. Ethyl allylacetate, b.p. 143–144°, n^{20}_D 1.4148, was obtained in 80% yield from allylacetic acid using the two-phase esterification procedure of Paul.[9] γ-Valerolactone was the principal by-product in the latter reaction.

Ethyl γ-(9,10-Dihydro-2-phenanthryl)-valerate (III). a. From Ethyl Allylacetate.—To a three-necked flask equipped with stirrer, condenser and aluminum chloride addition tube was added a mixture of 21.8 g. (0.12 mole) of 9,10-dihydrophenanthrene, 15.5 g. (0.12 mole) of ethyl allylacetate and 100 ml. of ethylene chloride. Aluminum chloride (25.8 g., 0.19 mole) was added at 0° over one-half hour and the dark brown complex was stirred at 0° for four hours and at room temperature for one-half hour. The mixture was poured onto an ice–hydrochloric acid mixture and after the usual workup the organic layer was distilled through a 29″ Podbielniak type column to give 4.6 g. of unreacted 9,10-dihydrophenanthrene, 12.4 g. of colorless ester, b.p. 197–207° (1 mm.), n^{20}_D 1.5813, $\lambda_{max.}$ 266 mμ (log ε 4.22).

Anal. Calcd. for $C_{21}H_{24}O_2$: C, 81.78; H, 7.84. Found: C, 82.01; H, 7.78.

On the basis of 9,10-dihydrophenanthrene consumed, the yield of ester III was 42%. When the reaction was carried out under similar conditions in nitrobenzene solvent, approximately 22% of the 9,10-dihydrophenanthrene, contaminated with considerable phenanthrene, was recovered. The product had b.p. 200–210° (0.7 mm.); n^{26}_D 1.6122, $\lambda_{max.}$ 252 mμ (log ε 4.43), and was obtained in only 15% yield.

b. **From γ-Valerolactone.**[10]—To a mixture of 18.0 g. (0.1 mole) of 9,10-dihydrophenanthrene and 15 g. (0.15 mole) of γ-valerolactone dissolved in 35 ml. of ethylene chloride was added 20 g. (0.15 mole) of aluminum chloride over about 10 minutes. The resultant dark brown complex was brought to reflux for three hours then hydrolyzed with ice and hydrochloric acid. The acidic material was extracted from the solvent with sodium carbonate solution which was subsequently acidified and the crude acid (20.2 g.) esterified in the usual manner. Distillation gave 7.6 g. of colorless ester, b.p. 185–188° (0.3 mm.), n^{20}_D 1.5815. The product had essentially the same infrared and ultraviolet absorption spectrum as the ester prepared from ethyl allylacetate.

The non-acidic material was chromatographed on alumina to give 5.2 g. of unreacted 9,10-dihydrophenanthrene so that the yield of ester III on the basis of starting material actually consumed was 32%.

A rapid Claisen distillation of the residue (12 g.) gave 5.8 g. of a pale yellow oil, b.p. 215–225° (0.2 mm.), n^{20}_D 1.5590; $\lambda_{max.}$ 257–260 mμ (log ε 4.18), 298 mμ (3.64). These constants, coupled with the analytical data, indicated that this was the dialkylated product, **2,7(?)-bis-(1-carbethoxy-3-butyl)-9,10-dihydrophenanthrene.**

Anal. Calcd. for $C_{28}H_{36}O_4$: C, 77.03; H, 8.31. Found: C, 76.68; H, 8.19.

c. **From β-(9,10-Dihydro-2-phenanthroyl)-propionic Acid (IV).**—The succinoylation of 9,10-dihydrophenanthrene was carried out as previously described[1] except for a change to ethylene chloride as solvent. A 90% yield of recrystallized acid IV, m.p. 153–157°, was obtained.

Ten grams (0.036 mole) of this acid was suspended in 600 ml. of anhydrous ether and to this slurry was added with stirring 75 ml. of methylmagnesium iodide solution (from 4.0 g. of magnesium and 20 g. of methyl iodide) over a period of about one hour. The resultant cream-colored suspension was allowed to stand two more hours at room temperature and then was heated for one-half hour on the steam-bath. The complex was decomposed in the usual manner, a trace of unreacted acid removed with sodium bicarbonate solution and the ether evaporated to give 7.2 g. (72%) of crude **γ-(9,10-dihydro-2-phenanthryl)-γ-valerolactone** (V), suitable for the reduction step. The analytical sample crystallized from methanol as colorless plates, m.p. 97–100°, $\lambda^{Nujol}_{max.}$ 5.69 μ, lit.[3] m.p. 61–70°.

Anal. Calcd. for $C_{19}H_{18}O_2$: C, 81.98; H, 6.52. Found: C, 81.71; H, 6.84.

To 14.0 g. (0.05 mole) of this lactone dissolved in 100 ml. of glacial acetic acid was added 10.6 g. (0.34 mole) of red phosphorus, 3.56 g. (0.014 mole) of iodine and 3.5 ml. of water. The mixture was heated under reflux for 20 hours, cooled and filtered through a sintered glass funnel. The filtrate was extracted thoroughly with ether and the combined extracts washed with sodium bisulfite solution followed by 10% sodium hydroxide. Evaporation of the ether left a trace of unreacted lactone. The basic extract was acidified and the oily acid taken up in ether and the solvent evaporated. Esterification of this crude material followed by distillation gave 10.0 g. (60% based on lactone V) of ester III, b.p. 198–205° (0.8 mm.), n^{20}_D 1.5822. The ultraviolet and infrared absorption spectra were essentially superimposable on those of the ester prepared from ethyl allylacetate.

Ethyl β-(9,10-Dihydro-2-phenanthryl)-butyrate (VI).—A three-necked flask was equipped as described for III and to it was added 25.2 g. (0.14 mole) of 9,10-dihydrophenanthrene, 28.0 g. (0.21 mole) of aluminum chloride and 80 ml. of hexane. A solution of 20.5 g. (0.18 mole) of ethyl vinylacetate in 50 ml. of hexane was added to this cooled slurry

---

[7] Melting points and boiling points are both uncorrected. Analyses are by Du-Good Labs., St. Louis 4, Mo., and Geller Labs., Hackensack, N. J. Infrared spectra were determined with a Perkin–Elmer model 21 double-beam spectrophotometer. The ultraviolet absorption spectra were measured in 95% ethanol using a Beckman model DU quartz spectrophotometer.

[8] E. Rietz, *Org. Syntheses*, **24**, 96 (1944).

[9] M. R. Paul, *Ann. chim.*, **18**, 303 (1932).

[10] Experiment conducted by D. E. Tuites.

over 15 minutes; the temperature rose from 5 to 10° during the addition. The brown complex was stirred for 18 hours at room temperature, decomposed in the usual manner and distilled to give 5.0 g. of unreacted 9,10-dihydrophenanthrene, b.p. 145–146° (5 mm.), and 14.0 g. (42%) of the ester as a colorless oil, b.p. 160–163° (0.2 mm.), $n^{22}\text{D}$ 1.5803, $\lambda_{\text{max.}}$ 266 mμ (log ϵ 4.10).

Anal. Calcd. for $C_{20}H_{22}O_2$: C, 81.60; H, 7.45. Found: C, 81.48; H, 7.53.

Ethyl β-(2-Phenanthryl)-butyrate (VII).—Ten grams (0.034 mole) of ester VI and 1.21 g. (0.038 mole) of recrystallized sulfur were heated in a test-tube at 250–270° for three hours. The crude reaction mixture was chromatographed on alumina in benzene–hexane (50:50) solution to give 8.9 g. (90%) of ester VII as a pale yellow oil, $n^{20}\text{D}$ 1.6315; $\lambda_{\text{max.}}$ (log ϵ) 254 (4.67); 278 (4.03); 298 (3.97); 322 (2.49); 334 (2.51); 350 (2.40). All attempts to crystallize the material failed.

Anal. Calcd. for $C_{20}H_{20}O_2$: C, 82.18; H, 6.90. Found: C, 81.95; H, 6.94.

1′-Keto-3′-methyl-1,2-cyclopentenophenanthrene (VIII).—Saponification of ester VII was carried out in the normal manner to give a 90% yield of crude acid, m.p. 100–112°, which was suitable for cyclization. This was accomplished by stirring 7.7 g. (0.029 mole) of the acid with 200 g. of polyphosphoric acid at 70° for 6 hours. The red solution was poured into water and the crude ketone extracted with ether. On standing, the ether solution deposited 0.3 g. of a pale yellow product, m.p. 201–202°, which formed bright yellow needles, m.p. 204–205°, on crystallization from ethyl acetate.

The main fraction was chromatographed on alumina using benzene–ether (95:5) as eluant. A small amount (0.6 g.) of a highly fluorescent oil preceded the main ketonic fraction which consisted of 5.4 g. (76%) of a pale yellow solid, m.p. 100–110°, suitable in purity for the next step. A small sample crystallized from propanol as warts, m.p. 132–134°; lit.[11] m.p. 135–136°.

Anal. Calcd. for $C_{18}H_{14}O$: C, 87.78; H, 5.73. Found: C, 87.48; H, 5.80.

The **2,4-dinitrophenylhydrazone** crystallized as red, powdery needles from ethyl acetate, m.p. 252–254° dec.

Anal. Calcd. for $C_{24}H_{18}N_4O_4$: C, 67.61; H, 4.25; N, 13.14. Found: C, 67.79; H, 4.28; N, 12.94.

3′-Methyl-1,2-cyclopentenophenanthrene (Diels Hydrocarbon) (IX).—The crude ketone from the cyclization (3.2 g., 0.013 mole) was dissolved in 25 ml. of diethylene glycol containing 2.0 g. of 85% hydrazine hydrate and the mixture was heated under reflux for three hours. Three grams of potassium hydroxide was added and the resultant orange solution heated to 185–190° for three hours. The dark brown mixture was poured into water and the crude hydrocarbon extracted with ether. The excess solvent was removed and the oil chromatographed on alumina using benzene–petroleum ether (50:50) as eluant. This gave 1.8 g. (60%) of the **Diels hydrocarbon (IX)**, as colorless plates, m.p. 123–125°, identical in all respects with an authentic sample,[12] m.p. 124–126°.

The **picrate** crystallized from ethanol as orange-brown needles, m.p. 116–118°, lit.[13] m.p. 117–118°.

Anal. Calcd. for $C_{18}H_{16}\cdot C_6H_3N_3O_7$: C, 62.47; H, 4.15. Found: C, 62.66; H, 4.27.

---

[11] E. Bergmann and H. Hilleman, *Ber.*, **66**, 1302 (1933).

[12] This sample of authentic Diels hydrocarbon was kindly supplied by Dr. Karl Miescher, Ciba A.-G., Basel, Switzerland.

[13] O. Diels, W. Gädke and P. Körding, *Ann.*, **459**, 1 (1927).

ITHACA, NEW YORK

[CONTRIBUTION NO. 127 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

The Catalytic Hydrogenation of the Benzene Nucleus. VIII. The Hydrogenation of Methyl-substituted Benzilic Acids

BY HILTON A. SMITH AND COMER D. SHACKLETT

RECEIVED FEBRUARY 8, 1954

Seventeen substituted benzilic acids have been hydrogenated in acetic acid solution over platinum catalyst, and the completely hydrogenated products isolated. The rate constants for the hydrogenations have been determined, and the influence of the number and position of substituents compared with earlier results dealing with the influence of substituents on the rate of hydrogenation of the benzene nucleus.

In an earlier publication the hydrogenation of compounds containing two benzene rings was discussed.[1] It was shown that many of these compounds underwent hydrogenation to form phenylcyclohexyl compounds and subsequently the dicyclohexyl derivatives, so that at the half hydrogenation point a pure compound could be obtained. In the case of benzilic acid, this is not found. Under the experimental conditions employed, the reaction mixture at the half-hydrogenation point contains about 65% of the phenylcyclohexylglycolic acid, with about 15% benzilic acid and 15% dicyclohexylglycolic acid.[2] Recently a number of methyl-substituted benzilic acids have been prepared,[3] and it seemed of interest to study the influence of the methyl substituents on the rate of catalytic hydrogenation of these compounds. The influence of the number and position of methyl substituents on the hydrogenation of benzene[4] and of benzoic acid[5] has already been reported.

Experimental

The syntheses of the 16 benzilic acids together with their physical constants, neutral equivalents and elemental analyses have been described.[3] The general experimental details for making hydrogenation runs and for calculating rate constants have been given in previous papers in this series. All hydrogenations were carried out in the presence of pure acetic acid and Adams platinum catalyst. All rate constants were corrected to the usual standard, and were comparable with previous data.

After complete hydrogenation, the products were precipitated from the reaction mixtures, after removal of the catalyst by filtration, by diluting the solutions with water. The products were then washed several times with water and dried in a vacuum desiccator over sodium hydroxide. A summary of the products, together with the neutral equivalents and melting points of the products is given in Table I. It should be recognized that the products may exist in several isomeric forms. The sharpness of the melting points indicates that in most cases a single isomer was present. In a few cases, the range in melting point indi-

---

[1] H. A. Smith, D. M. Alderman, C. D. Shacklett and C. M. Welch, THIS JOURNAL, **71**, 3772 (1949).

[2] H. A. Smith, C. D. Shacklett and C. M. Welch, *ibid.*, **74**, 4534 (1952).

[3] C. D. Shacklett and H. A. Smith, *ibid.*, **75**, 2654 (1953).

[4] H. A. Smith and E. F. H. Pennekamp, *ibid.*, **67**, 279 (1945)

[5] H. A. Smith and J. A. Stanfield, *ibid.*, **71**, 81 (1949).