Anal. Calcd. for $C_6H_9O_2Cl_3$: Cl, 48.46. Found: Cl, 48.97.

This ester (1.3 g.) was added to an ether solution of lithium aluminum hydride (10 ml., 0.5 *N*), and 1,3-dichloro-2-chloromethyl-2-hydroxymethylpropane (0.86 g., m.p. 64–65°, m.p. of mixture with an authentic sample[5] 64–65°) was obtained. This alcohol (0.4 g.) was then treated (2-hr. reflux) with thionyl chloride (1.5 g.) and pyridine (0.4 ml.) to give 1,3-dichloro-2,2-bis-(chloromethyl)-propane (0.35 g., m.p. 97–98°, m.p. of mixture with an authentic sample[5] 97–98°).

The identification of the product ester by the above method was tried because of the difficulty of its hydrolysis to the known tris-(chloromethyl)-acetic acid. It was recovered unchanged from three attempted hydrolyses: (1) with 2 *N* hydrochloric acid in aqueous methyl alcohol (50%, 17 hr. reflux), (2) with concentrated sulfuric acid (solution kept for 12 hr., and then added to water) and (3) with concentrated nitric acid (25%) in concentrated H_2SO_4 (steam-bath for 0.5 hr.). Treatment with ammonium hydroxide in aqueous methanol (50%, reflux for 12 hr.) gave no reaction, and reaction with 4 *N* sodium hydroxide in the aqueous methyl alcohol gave only water soluble products.

The Reaction of Diazomethane with Methyl α-Bromopropionate.—Methyl α-bromopropionate (177 g., 0.94 mole, illuminated in the mercury coil apparatus) was treated with diazomethane (18.6 g., 0.45 mole) as described above. The color of the latter disappeared from the solution 15 minutes after its addition was complete. Distillation of the reaction mixture gave unreacted methyl α-bromopropionate (160 g., b.p. 55–57° at 19 mm., n^{20}D 1.4464) and methyl β-bromoisobutyrate (16.6 g., b.p. 75–75.7° at 19 mm., n^{20}D 1.4550, 20% yield).

Anal. Calcd. for $C_5H_9O_2Br$: Br, 44.13. Found: Br, 44.11.

The product ester (1.0 g.) was treated (8 days at room temp.) with hydrochloric acid (10%) in aqueous methyl alcohol (50%). β-Bromoisobutyric acid (0.2 g., m.p. 15–17°) was isolated.

The Reaction of Diazomethane with Ethyl Bromoacetate.—This reaction with diazomethane (9.3 g., 0.225 mole) and the ester (220 g., 1.44 moles) was conducted as described above. The diazomethane color disappeared 40 minutes after its addition was complete. The product, ethyl β-bromopropionate, could not be separated from the unreacted ethyl bromoacetate by fractional distillation through the 12-plate Fenske column. The reaction mixture was distilled to give a mixture of the two esters (210 g., n^{20}D 1.4520). The distillation residue (21 g.) was distilled through a small Vigreux column to give a fraction (7 g., n^{20}D 1.4533, b.p. 48–60° at 10 mm.) and a tarry residue (14 g.). This liquid fraction was partially hydrolyzed with hydrobromic acid (20%) in aqueous methyl alcohol (50%). Unreacted ester (5.5 g.) was obtained, and the acid isolated was subjected to chromatographic separation on a silicic acid (Eimer and Amend) column using a benzene–ligroin (50%) solution. The first acidic product eluted was β-bromopropionic acid (1.3 g., m.p. 60.5–61.5°, m.p. of mixture with authentic sample 61°).

Reaction Rate and Inhibition Studies.—In a dark room, diazomethane (9.3 g., 0.225 mole) was swept by a stream of nitrogen into carbon tetrachloride (250 g., 1.60 mole) cooled to −22° in the previously described, mercury coil reaction vessel. After addition was complete, the reaction vessel and its contents were held at 0° in an ice–water-bath contained in a large dewar flask. A slow evolution of nitrogen occurred (see Fig. 2, after 35 min., 40 ml.; 250 min., 345 ml.).

A reaction mixture containing diazomethane (9.3 g., 0.225 mole) and carbon tetrachloride (300 g., 1.95 moles) was prepared as described above. The reaction vessel was then immersed in an ice–water-bath in an unsilvered dewar flask, and a 150-watt spotlight (held at a distance of 1 ft.) was turned on the flask. The evolution of nitrogen with time is given in Fig. 2. In 35 minutes, 4,365 ml. of nitrogen was obtained; and when the reaction was complete (140 min.), 5,880 ml. had evolved.

A rate study of the light-induced reaction of diazomethane (9.3 g., 0.225 mole) with ethyl bromoacetate (220 g., 1.23 moles) was conducted as described above. 5,630 ml. of nitrogen was obtained in 35 minutes, and 8,210 ml. had evolved when the reaction was complete (105 min., see Fig. 2).

A solution containing diazomethane (9.3 g., 0.225 mole), diphenylamine (5.0 g., 0.03 mole) and carbon tetrachloride (200 g., 1.30 mole) was illuminated as above with the 150-watt spotlight. After 18 hours the loss of the yellow diazomethane color was incomplete. The solution was distilled at reduced pressure. A yellow liquid, presumably diazomethane (3 ml.) condensed in the −80° trap. It evaporated completely on warming, and the vapor was conducted into a solution of 3,5-dinitrobenzoic acid (1.5 g.) in ether. Methyl 3,5-dinitrobenzoate (1.5 g., m.p. 106–107°, m.p. of mixture with an authentic sample 106–107°) was obtained. The distillation residue gave no 1,3-dichloro-2,2-bis-(chloromethyl)-propane.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS UNIVERSITY]

1-Hydroxy-11-methoxychrysene[1]

BY RODERICK A. BARNES AND MICHAEL A. MANGANELLI[2]

RECEIVED MAY 29, 1952

Proof has been obtained that 4-methoxyphenanthrene undergoes the Friedel–Crafts reaction at the 1-position. The ketoacid obtained by using succinic anhydride in the reaction has been reduced, cyclized and dehydrogenated to yield 1-hydroxy-11-methoxychrysene.

In connection with work on the preparation of hydroaromatic compounds related to steroids it was desirable to have available the completely aromatic analogs which could be used as reference compounds for structure proof by dehydrogenation. 1-Hydroxy-11-methoxychrysene, a previously unknown chrysene derivative, was of interest for this purpose.

4-Methoxyphenanthrene (I) was chosen as the starting material with the expectation that a Friedel–Crafts reaction with succinic anhydride would introduce the desired four-carbon chain at the 1-position. Mosettig and Duval[3] have previously carried out a reaction between I and acetyl chloride and obtained a ketone, x-acetyl-4-methoxyphenanthrene (m.p. 122.5–123.5°) which was different from the ketone (y-acetyl-4-methoxyphenanthrene, m.p. 80–81.5°) obtained by a Fries rearrangement of 4-phenanthryl acetate followed by methylation.

The reaction of I with succinic anhydride produced a single ketoacid (II) in 95% yield; this indicated that reaction had taken place almost exclu-

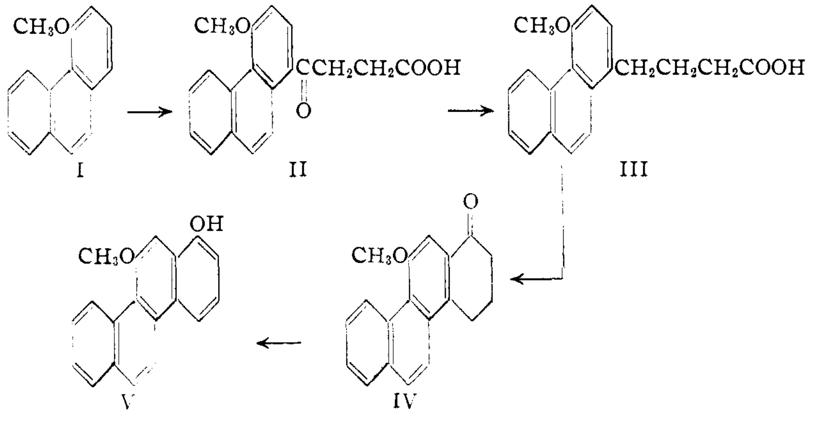
---

[1] Presented at the Meeting-in-Miniature of the North Jersey Section of the A.C.S., January 28, 1952.

[2] Abstracted from a thesis submitted by M. A. Manganelli to the Graduate Faculty of Rutgers University for the Ph.D. degree, January, 1952.

[3] E. Mosettig and H. Duval, THIS JOURNAL, **60**, 2409 (1938).

sively at a single position of the phenanthrene nucleus.[4]

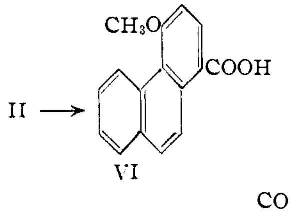


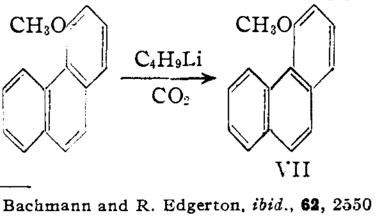
In order to prove that the succinoyl group of II was actually at the 1-position the keto group was reduced by the Clemmensen procedure and the resulting acid (III) cyclized with anhydrous hydrogen fluoride to yield IV. An unsuccessful attempt was made to convert IV to chrysene by a zinc dust distillation.

The structure of IV was finally established by reductive removal of the keto group followed by dehydrogenation. These reactions produced 5-methoxychrysene which was identical with an authentic sample[5] prepared by Cook and Schoental in an entirely different manner. 5-Methoxychrysene could have been formed only if the succinoyl group of II were at the 1- or 2-position. The 2-position is eliminated since it is meta to a methoxyl group and the Friedel–Crafts reaction would not be expected to introduce a succinoyl group at this position.

The dehydrogenation of IV with palladium black produced the desired 1-hydroxy-11-methoxychrysene although in rather low yield.

The proof of structure of our ketoacid (II) suggested that the x-acetyl-4-methoxyphenanthrene of Mosettig and Duval was actually 1-acetyl-4-methoxyphenanthrene. A confirmation of this was obtained by oxidative degradation of II. Acid VI had the same properties as those reported by Mosettig and Duval[3] for the acid obtained when x-acetyl-4-methoxyphenanthrene was subjected to the haloform reaction. An isomeric acid VII with quite different physical constants almost certainly had the carboxyl group at the 3-position since the lithium atom introduced by metalation enters an aromatic nucleus ortho to a methoxyl group wherever possible.





Experimental[6]

4-Methoxyphenanthrene (I).—This substance was prepared by the hydrogen fluoride cyclization of γ-(2-naphthyl)-butyric acid[7] to yield 4-keto-1,2,3,4-tetrahydrophenanthrene (90%) which was then dehydrogenated[8] (55%) and methylated (91%) essentially according to the procedures used by Mosettig and Duval.[3]

The 2,4-dinitrophenylhydrazone of 4-keto-1,2,3,4-tetrahydrophenanthrene melted at 259–260° after recrystallization from ethanol and ethyl acetate.

Anal. Calcd. for $C_{20}H_{16}O_4N_4$: C, 63.82; H, 4.29. Found: C, 63.78; H, 4.30.

The orange 2,4,7-trinitrofluorenone molecular complex of 4-methoxyphenanthrene melted at 198–199° after recrystallization from ethanol.

Anal. Calcd. for $C_{28}H_{17}N_3O_8$: C, 64.24; H, 3.27; N, 8.03. Found: C, 63.96; H, 3.27; N, 8.10.

β-(4-Methoxy-1-phenanthroyl)-propionic Acid (II).—A cold solution of aluminum chloride (19.6 g.) in nitrobenzene (70 ml.) was added with vigorous stirring to a mixture of (14 g.), nitrobenzene (70 ml.) and succinic acid (7.4 g.) at 0–5°. The reaction mixture was placed in the refrigerator for 48 hours and then decomposed with ice and hydrochloric acid. The nitrobenzene was steam distilled and the residue dissolved in sodium bicarbonate solution. Ether extraction removed any non-acidic substances and after acidification of the aqueous layer there was obtained 19.8 g. (95%) of II which melted at 190–193°. A sample for analysis was recrystallized from acetic acid and then from ethanol, m.p. 193–194.5°.

Anal. Calcd. for $C_{19}H_{16}O_4$: C, 74.01; H, 5.23. Found: C, 73.94; H, 5.30.

The methyl ester of II was prepared by treating the silver salt with methyl iodide. This substance melted at 116–117° after recrystallization from ligroin.

Anal. Calcd. for $C_{20}H_{18}O_4$: C, 74.52; H, 5.63. Found: C, 74.70; H, 5.31.

γ-(4-Methoxy-1-phenanthryl)-butyric Acid (III).—The Clemmensen reduction of II (19 g.) was allowed to proceed for 45 hours using amalgamated zinc (80 g.), glacial acetic acid (300 ml.), toluene (100 ml.) and hydrochloric acid (80 ml. and 5 additional 50-ml. portions). The crude product was methylated with dimethyl sulfate (30 ml.) and potassium hydroxide (44 g.) using acetone (160 ml.) and water (23 ml.) as the solvents. The alkaline solution remaining after completion of the methylation was diluted with water and acidified. The precipitate was filtered and recrystallized from glacial acetic acid. There was obtained 13.4 g. (74%) of II which melted at 171.9–172.1°.

Anal. Calcd. for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16. Found: C, 77.53; H, 6.06.

1-Keto-11-methoxy-1,2,3,4-tetrahydrochrysene (IV).—Acid III (10 g.) was cyclized with anhydrous hydrogen

---

[4] W. E. Bachmann and R. Edgerton, *ibid.*, **62**, 2550 (1940), have reported that 4-methylphenanthrene yields a mixture of keto acids in which the succinoyl group had entered both the 1- and 5-position of the phenanthrene nucleus.

[5] Kindly furnished by Prof. J. W. Cook; see J. W. Cook and R. Schoental, *J. Chem. Soc.*, 288 (1945).

[6] All melting points were determined on the Kofler hot-stage. Analyses were by J. F. Alicino, Metuchen, N. J., and W. Manser, Zurich, Switzerland.

[7] R. D. Haworth, *J. Chem. Soc.*, 1125 (1932); E. L. Martin, THIS JOURNAL, **58**, 1438 (1936).

[8] Freshly prepared palladium black is necessary for satisfactory results; a commercial catalyst gave almost none of the desired 4-phenanthrol.

fluoride (200 g.) as in the preparation of 4-ketotetrahydrophenanthrene. The crude ketone was purified by recrystallization from methanol. There was obtained 5.7 g. (61%) of product which melted at 148–148.5°.

Anal. Calcd. for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.59; H, 5.91.

The 2,4-dinitrophenylhydrazone melted at 286–287° after recrystallization from xylene.

Anal. Calcd. for $C_{25}H_{20}O_5N_4$: C, 65.78; H, 4.42. Found: C, 65.99; H, 4.59.

The 2,4,7-trinitrofluorenone molecular complex was prepared and recrystallized from absolute ethanol in the form of orange-red needles which melted at 194.5–195.0°.

Anal. Calcd. for $C_{32}H_{21}O_9N_3$: N, 7.10. Found: N, 7.20.

1-Hydroxy-11-methoxychrysene (V).—The dehydrogenation of ketone IV (500 mg.) was carried out using palladium black (75 mg.) with α-methylnaphthalene as the solvent. The crude base-soluble product was sublimed to yield 53 mg. (10%) of V which melted at 147–148° after one recrystallization from benzene-petroleum ether.

Anal. Calcd. for $C_{19}H_{14}O_2$: C, 83.19; H, 5.14. Found: C, 83.08; H, 5.12.

The melting point of a mixture of ketone IV and its dehydrogenation product V was 104–117°.

5-Methoxychrysene.—A mixture of ketone IV (1.5 g.), amalgamated zinc (4 g.) water (3 ml.), concentrated hydrochloric acid (9 ml.) and toluene (2 ml.) was refluxed for 90 hours; during this time six 3-ml. portions of hydrochloric acid were added. The crude product obtained by toluene extraction of the diluted reaction mixture was remethylated as in the preparation of III. The crude product thus obtained was purified by allowing a benzene solution to stand over sodium for 24 hours and then passing it through a column of alumina. Evaporation of the benzene eluates yielded as the first fraction a colorless solid[9] (m.p. above 200° with decomposition) which was not further characterized, then a solid, m.p. 108–115°, and finally a yellow oil. The second solid fraction (130 mg.) was dehydrogenated over palladium-on-charcoal (35 mg.) using α-methylnaphthalene as a solvent. The reaction mixture was diluted with petroleum ether, the catalyst filtered and the solution chilled to yield a pale yellow solid. This was recrystallized from benzene–petroleum ether to yield nearly colorless needles which melted at 139–141°. A mixture of this sample with authentic 5-methoxychrysene (m.p. 142–143°)[5] melted at 139–142°.

4-Methoxy-1-phenanthrenecarboxylic Acid (VI).—Acid II (320 mg.) was added to a suspension of calcium hypochlorite (1.5 g.) in water (145 ml.) and sodium carbonate (1.5 g.). The mixture was refluxed for five hours and filtered while hot. Sodium thiosulfate (7 g.) was added to the cold filtrate which then was acidified to yield a mixture of sulfur and crude acid VI. The acid was separated by extraction with sodium bicarbonate solution and reacidification of the clear extract. After recrystallization from toluene the pure acid melted at 237–239° (reported[8] melting point of 4-methoxy-x-phenanthrenecarboxylic acid was 238–239°). The methyl ester prepared by the action of diazomethane on VI melted at 91–92° after one recrystallization from methanol (reported[8] m.p. 93–94°).

4-Methoxy-3-phenanthrenecarboxylic Acid (VII).—A solution of butyllithium was prepared from lithium (0.35 g.), dry ether (25 ml.) and butyl chloride (3 g.). 4-Methoxyphenanthrene (0.5 g.) was added, the solution stirred for 12 hours and finally refluxed for 3 hours. The reaction mixture was poured into a slurry of Dry Ice (20 g.) in dry ether (50 ml.). The ether solution was warmed to room temperature, dilute hydrochloric acid was added and the ether layer separated. The acidic products were removed by sodium bicarbonate extraction. Acidification of the extracts yielded crude acid VII contaminated with valeric acid. The product was purified by recrystallization from benzene-ligroin, sublimation and recrystallization again, m.p. 154–155°.

Anal. Calcd. for $C_{16}H_{12}O_3$: C, 76.17; H, 4.80. Found: C, 76.12; H, 4.87.

NEW BRUNSWICK, NEW JERSEY

---

[9] D. Thomas and A. Nathan, THIS JOURNAL, **70**, 331 (1948), have obtained a diene, 7,7′-dimethoxy-3,3′,4,4′-tetrahydro-1,1′-binaphthyl as a by-product in the Clemmensen reduction of 7-methoxy-1-tetralone. The similarity in structure between this ketone and ketone IV suggests that an analogous diene might be formed from IV.

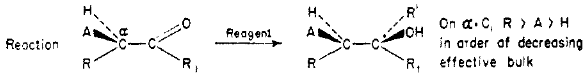
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA, LOS ANGELES]

Studies in Stereochemistry. X. The Rule of "Steric Control of Asymmetric Induction" in the Syntheses of Acyclic Systems

BY DONALD J. CRAM AND FATHY AHMED ABD ELHAFEZ

RECEIVED MARCH 12, 1952

A rule is proposed to correlate and predict the stereochemical direction of asymmetric induction in reactions of acyclic systems in which a new asymmetric center is created adjacent to an old: "In non-catalytic reactions of the type shown (Formulas), that diastereomer will predominate which would be formed by the approach of the entering group from the *least hindered side* of the double bond when the rotational conformation of the C–C bond is such that the double bond is flanked by the two least bulky groups attached to the adjacent asymmetric center." This rule successfully correlates the configurations of thirty-five compounds prepared by six different reactions of the above type, in each case the stereochemical relationships between the asymmetric carbons of the substances having been demonstrated by some independent means. This rule has been used to predict the configurations of fifty compounds whose stereochemical structures have been hitherto unknown.



The phenomenon of asymmetric induction in the synthesis of compounds that already contain one or more asymmetric carbon atoms has been recognized for many years, the classic work in acyclic systems being that of McKenzie.[1] Recently, four types of asymmetric synthesis have been reported in which symmetrical ketones have been reduced to optically active alcohols utilizing optically active reducing agents. Mosher, *et al.*, reduced methyl *t*-butyl ketone to active alcohol with active 2-methylbutylmagnesium chloride.[2] Doering, *et al.*, reduced isobutyrophenone with active 2-methyl-1-butanol (catalyzed with sodium ethoxide),[3a] 6-methyl-2-heptanone with active aluminum 2-

---

[1] (a) A. McKenzie, *J. Chem. Soc.*, **85**, 1249 (1904), and later papers. Other pertinent references are: (b) E. E. Turner and M. M. Harris, *Quarterly Reviews*, **1**, 299 (1947); (c) D. M. Bovey and E. E. Turner *J. Chem. Soc.*, 3223 (1951).

[2] H. S. Mosher and E. La Combe, THIS JOURNAL, **72**, 3994, 4991 (1950).

[3] (a) W. E. Doering and T. C. Aschner, *ibid.*, **71**, 838 (1949); (b) W. E. Doering and R. W. Young, *ibid.*, **72**, 631 (1950).