[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

Polynuclear Hydrocarbon Derivatives. X. Some Derivatives of 4,5-Dihydroacephenanthrylene[1]

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RECEIVED OCTOBER 22, 1957

The hydrocarbon obtained by treatment of 2-(5-acenaphthenyl)-5-methylhexane-2,5-diol (I) with boiling phosphoric acid has been shown to be 4,5-dihydro-7,8,10-trimethylacephenanthrylene (II) by independent synthesis *via* 10-methyl-(VIII) and 8,10-dimethyl-4,5,9,10-tetrahydro-7(8)-acephenanthrylenone (XII). Ketone VIII was prepared conveniently by the boron trifluoride-catalyzed condensation of acenaphthene with γ-valerolactone. Ketones VIII and XII also served as useful intermediates for the synthesis of 10-methyl-(XIX), 8,10-dimethyl-(XX) and 7,10-dimethyl-4,5-dihydroacephenanthrylene (XXI).

The novel single stage conversion of 2-methyl-5-phenylhexane-2,5-diol to 1,2,4-trimethylnaphthalene, under conditions of acid catalysis,[2] has led us to consider the possibility that polymethyl derivatives of more complex polynuclear hydrocarbons might be accessible in an equally direct manner through cyclodehydration of other analogous 1,4-diols.

The application of such a reaction to 2-(5-acenaphthenyl)-5-methylhexane-2,5-diol (I) has now yielded 4,5-dihydro-7,8,10-trimethylacephenanthrylene (II).

Diol I gave no significant amounts of picrate-forming hydrocarbons with either hydrogen fluoride or sulfuric acid, both of which convert 2-methyl-5-phenylhexane-2,5-diol to 1,2,4-trimethylnaphthalene.[2] However the milder reagent, boiling phosphoric acid, which yielded only dihydronaphthalene derivatives from 2-methyl-5-phenylhexane-2,5-diol, was sufficient to convert diol I to the fully aromatic hydrocarbon II in yields up to 20%. Other dehydrating agents were employed in a vain effort to obtain II in higher yields. Mild dehydration of diol I generally resulted in formation of the tetrahydrofuran III, often in excellent yield, while more severe treatment resulted in excessive polymerization.

Since the tetrahydrofuran forms so readily in the presence of acids, it is not unreasonable to suppose that III may be an intermediate in the conversion of I to II. Conversion of III to II with phosphoric acid, under the same conditions used with the diol, has demonstrated that such a path is at least possible.

An unequivocal synthesis of hydrocarbon II was achieved by a route similar to one which has been employed for synthesis of 1,2,4-trimethylnaphthalene.[3] The general plan required a good method of obtaining the unknown ketone VIII, which presumably could be converted to II through intermediates XII, XV and XVI.

Ketone VIII was obtained initially from acenaphthene in 43% over-all yield through intermediates IV (R = H), V and VII. Addition of methylmagnesium iodide to an ethereal suspension of keto acid IV (R = H) produced the lactone V in 74% yield.[4] Alkaline hydrolysis of V yielded hydroxy acid VI, which was characterized as the piperazinium salt. The free acid could not be purified because of its easy reversion to the lactone. However, when an alkaline solution of VI was subjected to high pressure catalytic hydrogenolysis, saturated acid VII was obtained in 79% yield.[5] Subsequent cyclization of VII with anhydrous hydrogen fluoride afforded a nearly quantitative yield of ketone VIII.

Synthesis of VIII by this sequence left little doubt as to its structure but did not provide a convenient source of the ketone in large quantity. Direct production of either acid VII or the ketone VIII itself from the catalyzed reaction of γ-valerolactone with acenaphthene appeared to be more promising. No such reaction has been described for acenaphthene, although reports of reactions of naphthalene,[6] 9,10-dihydrophenanthrene[7] and some simpler aromatic compounds[8,9] with lactones have appeared. Exploratory experiments with acenaphthene, γ-valerolactone and aluminum chloride in ethylene chloride showed that, as in the case of toluene,[10] *p*-alkylation occurred. However, acid VII was produced in only low yield, accompanied by higher-boiling acids which presumably resulted from polyalkylation. When the reaction of acenaphthene with γ-valerolactone was catalyzed with boron trifluoride, ketone VIII was produced directly in 18–20% yields. Purification was easy since only trace amounts of other substances were formed and no acid VII was found in the reaction mixture.

The next requirement was the substitution of a single methyl group in the 8-position of the ketone VIII. The most reliable method for such a monomethylation appears to be that first worked out by Kötz and Michels,[11] and subsequently improved by Bachmann and Thomas.[12] The method was employed, with only minor modifications, for the preparation of the 8,10-dimethyl ketone XII from ketone VIII with an over-all yield of 60%, and the

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(1) Abstracted from the Ph.D. dissertation of Robert C. Petterson. Presented before the Organic Chemistry Division, American Chemical Society, Miami, Fla., April, 1957. Previous papers in this series include M. C. Kloetzel and W. Close, *J. Org. Chem.*, **11**, 395 (1946); M. C. Kloetzel and H. L. Herzog, *ibid.*, **15**, 370 (1950); M. C. Kloetzel and H. L. Herzog, THIS JOURNAL, **72**, 1991 (1950); M. C. Kloetzel, W. King and J. H. Menkes, *ibid.*, **78**, 1165 (1956).

(2) M. C. Kloetzel, *ibid.*, **62**, 3405 (1940).

(3) M. C. Kloetzel, *ibid.*, **62**, 1708 (1940).

(4) Compare P. K. Porter, *ibid.*, **45**, 1086 (1923), and L. F. Fieser and M. S. Newman, *ibid.*, **58**, 2376 (1936).

(5) Compare W. S. Johnson, A. Goldman and W. P. Schneider, *ibid.*, **67**, 1357 (1945).

(6) E. J. King, *ibid.*, **49**, 562 (1927).

(7) D. D. Phillips and E. J. McWhorter, *ibid.*, **76**, 4948 (1954).

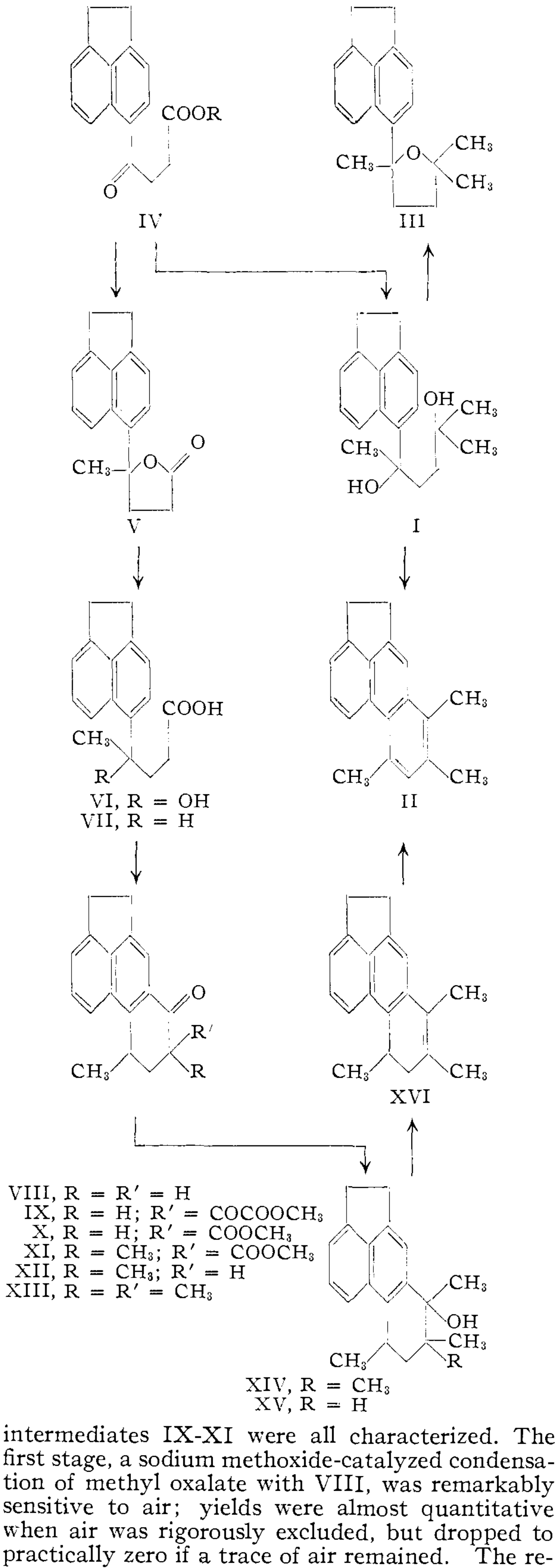
(8) R. V. Christian, Jr., *ibid.*, **74**, 1591 (1952).

(9) W. E. Truce and C. E. Olson, *ibid*, **74**, 4721 (1952).

(10) D. D. Phillips, *ibid.*, **77**, 3658 (1955).

(11) A. Kötz and A. Michels, *Ann.*, **350**, 204 (1906).

(12) W. E. Bachmann and D. G. Thomas, THIS JOURNAL, **63**, 598 (1941).



VI, R = OH
VII, R = H

VIII, R = R′ = H
IX, R = H; R′ = COCOOCH₃
X, R = H; R′ = COOCH₃
XI, R = CH₃; R′ = COOCH₃
XII, R = CH₃; R′ = H
XIII, R = R′ = CH₃

XIV, R = CH₃
XV, R = H

intermediates IX-XI were all characterized. The first stage, a sodium methoxide-catalyzed condensation of methyl oxalate with VIII, was remarkably sensitive to air; yields were almost quantitative when air was rigorously excluded, but dropped to practically zero if a trace of air remained. The resulting glyoxylate IX was heated with powdered glass to give keto ester X, which was methylated to produce XI. Two forms of the dimethyl ketone XII were obtained on hydrolysis and decarboxylation of ester XI. The major product (77% yield) melted at 114–114.5°, after melting and resolidifying at 104–105°. The minor product crystallized from the mother liquors of the major product in about 8% yield. One crystallization gave a sample, m.p. 103–105°, which depressed the m.p. of the higher-melting form, but during a second crystallization the material was converted to the higher-melting form.

Direct methylation of ketone VIII was investigated, in an effort to obtain XII more conveniently. Direct methylation of ketones having a methylene group adjacent to the carbonyl function commonly results in the formation of a mixture of mono- and dimethylated products[13] or dimethylation only.[14] In the hope that a separable mixture would result, the 10-methyl ketone VIII was treated with potassium *t*-butoxide and methyl iodide. The product was the 8,8,10-trimethyl ketone XIII and no XII could be detected. Ketone XII likewise yields XIII upon treatment with potassium *t*-butoxide and methyl iodide. Ketone XIII is stable under alkaline conditions and yields a stable crystalline carbinol XIV upon treatment with methylmagnesium iodide.

Grob and Jundt[14] have solved ingeniously a similar synthetic problem. They found that reaction of a β-tetralone with an equimolar amount of potassium metal in benzene resulted in the separation of the monopotassium salt, and that the resulting slurry reacted with methyl iodide to form the desired monomethyl ketone in excellent yield. When this method was applied to ketone VIII, similar behavior was observed, and a 14% yield of XII was isolated. The rather selective method of monomethylation recently reported by Stork, Terrell and Szmuszkovicz[15] was not applied to VIII since this ketone did not react to any significant extent with pyrrolidine under the usual conditions.

The 4,5-dihydro-7,8,10-trimethylacephenanthrylene (II) was made easily from ketone XII by conventional methods. Dehydration with formic acid of the crude carbinol XV, prepared from XII and methylmagnesium iodide, gave XVI in 53% yield. This olefin was dehydrogenated to II by palladium-on-charcoal at 285° under nitrogen and also by chloranil at 140°. The catalytic method gave the better yield (92%). For preparative purposes it was found best to omit isolation of the olefin, which is sensitive to air and to acids. Merely heating the crude carbinol with catalyst afforded II directly in 45% over-all yield from ketone XII. The identity of this dehydrogenation product with the aromatic compound from cyclodehydration of diol I was established by comparison of their infrared spectra and by the mixed melting points of the hydrocarbons themselves, their picrates and their 2,4,7-trinitrofluorenone derivatives.

Thus, 4,5-dihydro-7,8,10-trimethylacephenanthrylene (II) now has been made available from acenaphthene *via* a sequence requiring isolation of only

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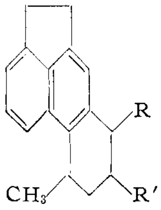
(13) W. J. Bailey and M. Madoff, THIS JOURNAL, **76**, 2707 (1954).

(14) C. A. Grob and W. Jundt, *Helv. Chim. Acta*, **31**, 1691 (1948).

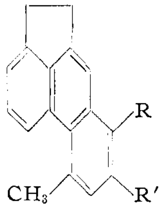
(15) G. Stork, R. Terrell and J. Szmuszkovicz, THIS JOURNAL, **76**, 2029 (1954).

two intermediates (VIII and XII) and also *via* diol I by a four-stage sequence.

The availability of ketones VIII and XII made it a simple matter to prepare three additional methyl-substituted dihydroacephenanthrylenes. These ketones were reduced to hexahydroacephenanthrylenes XVII and XVIII, respectively, by the Wolff–Kishner method. XVII hydrocarbon afforded a trinitrofluorenone derivative but not a stable picrate. Dehydrogenation of XVII and XVIII at 310° over palladium-on-charcoal catalyst produced 10-methyl- (XIX) and 8,10-dimethyl-4,5-dihydroacephenanthrylene (XX), respectively, in nearly quantitative yields. 7,10-Dimethyl-4,5-dihydroacephenanthrylene (XXI) was obtained when the crude reaction product from ketone VIII and methylmagnesium iodide was similarly dehydrogenated.



XVII, R = R′ = H
XVIII, R = H; R′ = CH_3



XIX, R = R′ = H
XX, R = H; R′ = CH_3
XXI, R = CH_3; R′ = H

Acknowledgment.—R. C. P. wishes to thank Dr. Robert C. Ferris for encouragement and the Purex Corporation, Ltd., for assistance under its educational benefits program.

Experimental[16]

Lactone of γ-Hydroxy-γ-methyl-5-acenaphthenebutyric Acid (V).—An ether solution of the Grignard reagent from 2.42 g. of magnesium and excess methyl iodide was added over a period of 2 hours to a stirred suspension of 10 g. of finely powdered γ-oxo-5-acenaphthenebutyric acid[17] (IV, R = H) in 160 cc. of anhydrous ether (nitrogen atmosphere). After 18 hours of stirring at room temperature (somewhat lower yields if at 0° or 35°) and subsequent hydrolysis with ice and hydrochloric acid, 1 g. of unchanged IV (R = H) was recovered by extraction of the organic layer with aqueous sodium carbonate. Spontaneous evaporation of the washed and dried ether layer gave 8.4 g. of crystalline lactone. Recrystallization from a mixture of petroleum ether (b.p. 63–69°) and acetone yielded 7.4 g. (74%) of colorless plates, m.p. 101–110°. A sample crystallized from aqueous alcohol melted at 104–105° after drying *in vacuo*. The m.p. slowly changed to 111–113° as the sample was allowed to stand. This lactone gave a positive Feigl test,[18] imparted a violet color to concentrated sulfuric acid and dissolved slowly in hot 1 *N* sodium hydroxide.

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found (form, m.p. 104–105°): C, 80.95; H, 6.44. Found (form, m.p. 111–113°): C, 81.11; H, 6.43.

γ-Hydroxy-γ-methyl-5-acenaphthenebutyric Acid (VI).—A crude crystalline sample of the hydroxy acid was obtained when a solution made by warming a sample of the lactone with 10% potassium hydroxide was neutralized exactly in the cold. The solid was filtered off rapidly, 1 g. of it was dissolved in a solution of piperazine hexahydrate (0.4 g.) in ethanol (50 cc.) and the solution was allowed to stand for several days. Evaporation yielded the piperazinium salt as an oil which soon crystallized. Recrystallization from a mixture of ethanol and acetone (1:1) gave small colorless prisms, dec. 162–163° (when placed in a bath at 155° and heated at the rate of 2°/min.). The decomposition temperature depended on the mode of heating.

Anal. Calcd. for $C_{38}H_{46}N_2O_6$: C, 72.82; H, 7.40. Found: C, 72.89; H, 7.42.

γ-Methyl-5-acenaphthenebutyric Acid (VII).—A slightly alkaline solution was made from lactone V (8.7 g.) and dilute aqueous sodium hydroxide. Copper chromite catalyst Cu-0102-P[16] (2.1 g.) was added, and the mixture was subjected to an initial hydrogen pressure of 120 atmospheres at room temperature. After heating for 7 hours at 135°, and working up in the usual manner,[5] there was obtained 6.9 g. (79%) of once-distilled oily VII, b.p. 195–200° (1–2 mm.), suitable for use in the next reaction. The anilide[19] separated from aqueous ethanol in colorless needles, m.p. 130.5–132°.

Anal. Calcd. for $C_{23}H_{23}NO$: C, 83.85; H, 7.04. Found: C, 83.89; H. 7.11.

10-Methyl-4,5,9,10-tetrahydro-7(8)-acephenanthrylenone (VIII). (a) **From Cyclization of γ-Methyl-5-acenaphthenebutyric Acid (VII).**—Evaporation of a solution of 1.85 g. of acid VII in anhydrous hydrogen fluoride yielded 1.60 g. (93%) of ketone VIII, m.p. 114–118°. Two crystallizations from ethanol (Nuchar C) gave pale yellow needles, m.p. 121.0–121.5°. The m.p. slowly changed to 124–125° during storage. The ketone showed infrared absorption at 1664, 1604, 1330m, 1278w, 1254w, 1238m, 1185, 1155m, 1124w, 1093w, 1055w, 1016m, 897, 892, 881, 857m, 833m, 788, 768 and 754 cm.$^{-1}$.

Anal. Calcd. for $C_{17}H_{16}O$: C, 86.40; H, 6.82. Found: C, 86.72; H, 6.90.

The oxime crystallized from aqueous ethanol in colorless needles, m.p. 186–189° dec.

Anal. Calcd. for $C_{17}H_{17}NO$: C, 81.24; H, 6.82. Found: C, 81.32; H, 6.84.

(b) **From Acenaphthene and γ-Valerolactone.**—A stirred mixture of technical acenaphthene (115 g., 0.75 mole) and γ-valerolactone (50 g., 0.5 mole) was heated to 90° and then saturated with boron trifluoride during 40 min. at 90–110° (about 0.5 mole was absorbed). The vessel was stoppered and heated on a steam-bath for 16 hours, boron trifluoride being bubbled into the melt for 10-minute periods at the end of the 1st and 2nd hours. The mixture was poured into water, dilute potassium hydroxide and benzene (300 cc.) were added, the filtered organic layer was washed with 10% potassium hydroxide and water, and the solution was then distilled *in vacuo* to give 66 g. of unchanged acenaphthene and 32 g. of crude ketone VIII, b.p. 195° (2 mm.). Redistilled ketone was crystallized from ethanol and from a mixture of acetone and ethanol (5:1): yield 23.5 g. (20%), m.p. 120–122.5°. Recrystallization gave colorless soft needles, m.p. 124–125°, undepressed by admixture with a sample prepared by method a.

About 0.5 g. of an unidentified ketone, m.p. 146–156°, was obtained from the mother liquors. Recrystallization from benzene, acetone and ethanol gave yellow prisms, m.p. 154.5–156.0°, but the substance was not analytically pure.

Yields of ketone VIII were not improved by using purified starting materials, changing the reaction time to either 28 hours or 6 hours, or by adding 0.25 mole of phosphorus pentoxide[20] per mole of lactone. In the best of several experiments with aluminum chloride catalysis, a solution of acenaphthene (77 g.) and γ-valerolactone (10 g.) in *sym*-tetrachloroethane (320 cc.) was treated with aluminum chloride (16.7 g.) and heated to 57° for 13 hours. After hydrolysis 9 g. of brown acidic gum was extracted with 20% sodium carbonate (no ketone was found), distilled, and allowed to react with anhydrous hydrogen fluoride. The yield of ketone VIII, m.p. 119–121°, was only 0.24 g. (1%).

Methyl 4,5,7,8,9,10-Hexahydro-10-methyl-7-oxo-8-acephenanthryleneglyoxylate (IX).—Condensation of ketone VIII (7.1 g.) with methyl oxalate by adaptation of the

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[16] Melting points are uncorrected. Microanalyses are by Dr. Adalbert Elek, Elek Microanalytical Laboratories, Los Angeles, Calif., and by William Schenck, formerly of the University of Southern California. Infrared spectra (Nujol mulls) are by Upendra K. Pandit, using a Perkin–Elmer model 13 spectrophotometer. We are indebted to the Victor Chemical Works for a gift of polyphosphoric acid and to the Harshaw Chemical Co. for a gift of copper chromite.

[17] L. F. Fieser, *Org. Syntheses*, **20**, 1 (1940).

[18] D. Davidson, *J. Chem. Educ.*, **17**, 81 (1940).

[19] S. M. McElvain, "The Characterization of Organic Compounds," The Macmillan Co., New York, N. Y., 1946, p. 184.

[20] C. E. Welsh and G. F. Hennion, THIS JOURNAL, **63**, 2603 (1941).

method of Bachmann, Cole and Wilds[21] gave 9.4 g. of glyoxylate IX, m.p. 165° dec. Yields were very low if air was not rigorously excluded. Crystallizations from acetone and benzene gave bright yellow blades, m.p. 174–175° (Pyrex capillary). The glyoxylate gave a dark green color with alcoholic ferric chloride, and a red color with concentrated sulfuric acid, which rapidly became purple, then green-brown.

Anal. Calcd. for $C_{20}H_{18}O_4$: C, 74.52; H, 5.63. Found: C, 74.71; H, 5.48.

A mixture of the aforementioned glyoxylate (31.5 g.) and powdered soft glass (16 g.) was heated in a nitrogen atmosphere to 130–140° for 1 hour and then briefly to 160°. Extraction with benzene afforded 15.1 g. (53%) of **methyl 4,5,7,8,9,10-hexahydro-10-methyl-7-oxo-8-acephenanthrylenecarboxylate** (X), m.p. 131–135°, and a second crop of 5.8 g. (20%) of X, m.p. 127–130°, suitable for methylation. An analytical sample separated from methanolic acetone in faintly yellow prisms, m.p. 133.5–134.5°, and gave a green color with ethanolic ferric chloride.

Anal. Calcd. for $C_{19}H_{18}O_3$: C, 77.53; H, 6.16. Found: C, 77.62; H, 6.37.

Methylation[21] of crude keto ester X (6.1 g.) gave 6.1 g. (95%) of **methyl 8,10-dimethyl-4,5,7,8,9,10-hexahydro-7-oxo-8-acephenanthrylenecarboxylate** (XI), m.p. 167–173°. Recrystallization from methanolic acetone produced long colorless prisms, m.p. 174.5–176° after being dried in vacuum at 77°. The compound gave no color with ethanolic ferric chloride, but gave a deep red color with concentrated sulfuric acid.

Anal. Calcd. for $C_{20}H_{20}O_3$: C, 77.90; H, 6.54. Found: C, 77.95; H, 6.82.

8,10-Dimethyl-4,5,9,10-tetrahydro-7(8)-acephenanthrylenone (XII). (a) **From XI.**—Hydrolysis and decarboxylation of ester XI (6.16 g.) with a boiling solution of potassium hydroxide in aqueous methanol[21] appeared to be complete within 2.5 hours. Crude ketone which separated during the reaction was crystallized from ethanol (50 cc.); yield 3.85 g. (77%) of colorless microcrystals, m.p. 112–113° after prior melting and resolidification at about 103.5°. Additional crops (8%) of lower-melting material attained the same m.p. after recrystallization. A final crystallization from methanol yielded colorless needles, m.p. 114–114.5° with prior melting and resolidification at 104–105°. This ketone did not decolorize bromine in carbon tetrachloride nor did it give a color with alcoholic ferric chloride. With sulfuric acid a bright orange color was produced.

Anal. Calcd. for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.26; H, 7.53.

(b) **From VIII.**—To 0.40 g. of metallic potassium in 20 cc. of dry toluene was added 2.21 g. of ketone VIII. The mixture was heated to reflux for 1 hour (nitrogen atmosphere), then treated with 5 cc. of methyl iodide and heated to reflux for 75 min., and finally allowed to stand at room temperature overnight. Ether, water, 10% sulfuric acid and sodium bisulfite were added successively. Evaporation of the washed and dried organic layer yielded 2.3 g. of a gum, which was distilled *in vacuo*, and crystallized from 100% ethanol to yield 0.32 g. (14%) of ketone XII, m.p. 99–102°. Recrystallization from ethanol gave stout needles, m.p. 111–112° alone, and 111–112° with prior melting and resolidification at 105° when mixed with ketone prepared by method a.

8,8,10-Trimethyl-4,5,9,10-tetrahydro-7(8)-acephenanthrylenone (XIII). (a) **From Ketone VIII.**—To a stirred ice-cold solution made from 3.8 g. (0.096 mole) of potassium metal and 100 cc. of dry *t*-butyl alcohol was added rapidly an ice-cold solution of 7.5 g. (0.032 mole) of ketone VIII in 120 cc. of dry benzene. Methyl iodide (13.6 g., 0.096 mole) was added and the mixture was kept at 0–5° for 2 hr., then at room temperature for 2 hr., and finally was heated to 50° for 5 min. Addition of water to the cooled mixture, followed by extraction with benzene and subsequent distillation of the washed and dried extracts *in vacuo*, gave 6.7 g. of orange oil, b.p. 205–210° (1 mm.), and 1.0 g. of undistillable residue. From a solution of the distillate in hot 95% ethanol (100 cc.), 2.9 g. (35%) of ketone XIII separated in 2 days at room temperature; m.p. 97–101°, which was raised to 104.5–106.5° by two crystallizations from methanol. An analytical sample (colorless rods from ethanol) melted at 105.5–106.5° after drying in vacuum at 78° and showed infrared absorption at 1667, 1603m, 1315m, 1302m, 1256w, 1233m, 1185, 1175, 1071m, 1040m, 1011w, 972m, 903m, 885, 858m, 835w, 789m, 771 and 741w cm.$^{-1}$.

Anal. Calcd. for $C_{19}H_{20}O$: C, 86.32; H, 7.62. Found: C, 86.10; H, 7.24.

When ketone XIII was mixed with ketone XII the m.p. was strongly depressed. No ketone XII could be isolated from the aforementioned methylation reaction. Ketone XIII (no α-hydrogen) was recovered nearly quantitatively from a 1.3 *M* potassium *t*-butoxide solution in *t*-butyl alcohol after a week at room temperature, conditions which converted ketone XII into an intractable gum.

(b) **From Ketone XII.**—Methylation of ketone XII (1.00 g.) under the conditions described in (a) gave a gum from which was obtained, after sublimation *in vacuo* and crystallization from alcohol, 0.60 g. (57%) of ketone XIII in prisms, m.p. 102–105°, undepressed by admixture with XIII prepared from ketone VIII.

The reaction of ketone XIII with excess methylmagnesium iodide under the usual conditions[3] gave a quantitative yield of **7-hydroxy-4,5,7,8,9,10-tetramethylacephenanthrylene** (XIV) as a readily crystallizable gum. Recrystallization from a mixture of ether and petroleum ether, or from methanol, or from aqueous methanol gave shiny, colorless blades, m.p. 133.5–135°; drying over phosphorus pentoxide in a vacuum raised the m.p. to 135–137°. This carbinol gave a purple color with concentrated sulfuric acid.

Anal. Calcd. for $C_{20}H_{24}O$: C, 85.67; H, 8.63. Found: C, 85.60; H, 8.62.

7,8,10-Trimethyl-4,5,9,10-tetrahydroacephenanthrylene (XVI).—Ketone XII reacted smoothly with methylmagnesium iodide[3] to give a quantitative yield of a gum, presumably the trimethylcarbinol XV. Olefin XVI was obtained as colorless crystals, m.p. 67–79° (1.88 g.), when the crude carbinol (2.13 g.) was shaken for 1 hr. with 90% formic acid. Crystallization from ethanol was accompanied by darkening of the hot solutions and was best done under nitrogen; yield 0.85 g. (43%) of yellow crystals, m.p. 90–92° (with previous softening), and an additional 0.20 g. (10%), m.p. 84–90°, by crystallization of a sublimate of the residue from evaporation of the mother liquor. Pure olefin XVI crystallized from ethanol in dense colorless prisms, m.p. 94–95°, which very slowly decolorized a solution of potassium permanganate in aqueous acetone.

Anal. Calcd. for $C_{19}H_{20}$: C, 91.88; H, 8.12. Found: C, 91.72; H, 8.40.

When the residue from evaporation of the mother liquor from the aforementioned material melting at 84–90° was heated with a saturated solution of picric acid in ethanol there was obtained a red picrate (12 mg.), m.p. 185.5–186°, identified as the picrate of 4,5-dihydro-7,8,10-trimethylacephenanthrylene by mixed m.p. with authentic picrate. Olefin XVI formed no picrate under similar conditions.

4,5-Dihydro-7,8,10-trimethylacephenanthrylene (II). (a) **By Catalytic Dehydrogenation of XVI.**—A mixture of freshly recrystallized olefin XVII (428 mg.) with 10% palladium-on-charcoal catalyst under a gentle stream of nitrogen was heated from 200 to 285° in 15 minutes, and at 285° for 30 minutes; yield 390 mg. (92%) of hydrocarbon II, m.p. 137–143°, which crystallized from acetone or acetonitrile in shiny, colorless blades, m.p. 144–145°.

Anal. Calcd. for $C_{19}H_{18}$: C, 92.64; H, 7.36. Found: C, 92.37; H, 7.63.

The picrate separated from benzene in red needles, m.p. 186°.

Anal. Calcd. for $C_{25}H_{21}N_3O_7$: N, 8.84. Found: N, 8.80.

The 2,4,7-trinitrofluorenone derivative crystallized in red needles from benzene, m.p. 196–197°.

Anal. Calcd. for $C_{31}H_{23}N_3O_7$: N, 7.65. Found: N, 7.79.

(b) **By Dehydrogenation of XVI with Chloranil.**—It was established by mixed melting point determination that the product obtained by heating a solution of equimolar quantities of olefin XVI and chloranil in xylene[22] was identical with II prepared as described in (a); the yield was 55%.

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[21] W. E. Bachmann, W. Cole and A. L. Wilds, THIS JOURNAL, **62**, 825 (1940).

[22] N. Dost and K. van Nes, *Rec. trav. chim.*, **70**, 403 (1951).

(c) **Directly from Ketone XII.**—A mixture of crude carbinol XV (142 mg.), obtained from the reaction of ketone XII with methylmagnesium iodide, with 10% palladium-on-charcoal catalyst (21 mg.) was heated under a nitrogen atmosphere to 260° in 20 min., to 310° during the next 0.5 hr., and at 310° for 0.5 hr. The organic products were removed with benzene and sublimed at 140° (1 mm.), which gave 84 mg. of crude hydrocarbon II, m.p. 120–131°. Recrystallization from acetone gave 50 mg. (38%), m.p. 140–144°, and 9 mg. (7%) of less pure II, m.p. 135–138°.

2-(5-Acenaphthenyl)-5-methylhexane-2,5-diol (I).—To the Grignard reagent from magnesium (7.29 g.), methyl iodide (43 g.) and ether (150 cc.), cooled in an ice-bath, a solution of methyl γ-oxo-5-acenaphthenebutyrate (IV, R = CH_3; 13.4 g.) in benzene (60 cc.) was added dropwise with vigorous stirring. After 2 hr. at room temperature the clear solution was treated with ice and dilute ammonium chloride solution. The organic layer was washed with water, 5% acetic acid, 5% sodium bicarbonate solution and finally with water, was dried (Drierite), and was allowed to evaporate spontaneously. The resulting oil crystallized when triturated with ether and petroleum ether (b.p. 35–60°), giving 7.22 g. of colorless crystalline diol; one crystallization from a mixture of acetone and petroleum ether gave 6.1 g. (43%), m.p. 123–125°. A sample recrystallized for analysis from the same mixture melted at 125–126°.

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.55; H, 7.76.

While our work was in progress Roger and Shepherd[23] described the synthesis of diol I from IV (R = C_2H_5) by a similar method in 32% yield, and reported the m.p. as 124–126°.

Dehydration of Diol I. (a) **To 4,5-Dihydro-7,8,10-trimethylacephenanthrylene** (II).—A mixture of 2-(5-acenaphthenyl)-5-methylhexane-2,5-diol (3 g.) and 85% phosphoric acid (7.5 cc.) was heated to reflux for 48 hr., and was then cooled and diluted with water. An ether extract of the resulting mixture was washed with aqueous sodium bicarbonate, dried and evaporated. The ethanol-soluble portion of the residual gum was sublimed at 1 mm. pressure, and then crystallized from acetone to yield 187 mg. of crude hydrocarbon II, m.p. 134–141°. Additional hydrocarbon was obtained by replacement of the acetone in the mother liquors with hot benzene and addition of picric acid (0.3 g.); 190 mg. of crude picrate of II crystallized, m.p. 180–183°, and was decomposed on an alumina column. After recrystallization the hydrocarbon melted at 144–145°, its picrate at 186–187°, and the 2,4,7-trinitrofluorenone derivative at 195–196°; these melting points were not depressed by admixture with authentic samples obtained from the aforementioned synthesis. The hydrocarbons likewise displayed identical infrared spectra. Yields in this reaction varied from 5 to 20% and were not improved by shortening the reaction time to 24 hr. or by reducing the concentration of the phosphoric acid to 75%. A small amount of by-product, possibly a polymer of a tetrahydrotrimethylacephenanthrylene, was isolated in the form of pale yellow prisms, m.p. 323–326° (under nitrogen).

Anal. Calcd. for $(C_{19}H_{20})_n$: C, 91.88; H, 8.12. Found: C, 91.88; H, 8.29.

(b) **To Tetrahydro-2-(5-acenaphthenyl)-2,5,5-trimethylfuran** (III).—A solution of diol I (1 g.) in saturated ethanolic picric acid was heated to reflux for 24 hr., then evaporated, neutralized with sodium bicarbonate, and extracted with ether. Evaporation of the ether solution left 0.90 g. (95%) of crystalline tetrahydrofuran III, m.p. 59–66°. Recrystallization from ethanol gave colorless plates, m.p. 68–70°. The compound does not form a stable picrate.

Anal. Calcd. for $C_{19}H_{22}O$: C, 85.67; H, 8.32. Found: C, 85.71; H, 8.36.

While this work was in progress Roger and Shepherd[23] described the preparation of III from diol I in unstated yield, and reported the m.p. as 68.5–69°. We found the furan III to be the major product from the reaction of I with several other mild dehydrating agents.

When III (3.6 g.) was heated to reflux for 48 hr. with 85% phosphoric acid, there was obtained 320 mg. (5%) of the picrate of hydrocarbon II, m.p. 179–186°. The purified picrate did not depress the m.p. of authentic picrate of II.

(c) **To a Dimer** $(C_{19}H_{18})_2$.—When a mixture of diol I (1 g.) and polyphosphoric acid[16] (15 cc.) was heated with stirring under nitrogen for 6 hr. at 180°, and then worked up by the method described in (a) for reaction of the diol with phosphoric acid, none of the hydrocarbon II was found. The products consisted of tar, small amounts of unidentified picrate-forming substances, and 95 mg. of yellow crystals, m.p. 169–174° (with previous softening). Recrystallization of the latter from ethanol gave bright yellow crystals, m.p. 173–175.5°. This compound formed no picrate and gave a negative Baeyer test for unsaturation.

Anal. Calcd. for $(C_{19}H_{18})_2$: C, 92.63; H, 7.37; mol. wt., 492. Found: C, 92.68; H, 7.15; mol. wt. (cryoscopic), 514.

(d) **To a Polymer** $(C_{19}H_{20})_n$.—A mixture of diol I (7.4 g.), concentrated sulfuric acid (5 cc.), acetic anhydride (5 g.) and acetic acid (50 cc.) was allowed to stand for 3 days at room temperature. Crystallization of the ethanol-soluble portion (1 g.) of the products yielded a polymer of unknown structure which decomposed at 247.5–249°.

Anal. Calcd. for $(C_{19}H_{20})_n$: C, 91.88; H, 8.12. Found: C, 91.89; H, 8.27.

Synthesis of 4,5-Dihydro-10-methylacephenanthrylene (XIX).—The Huang-Minlon modification[24] of the Wolff–Kishner reduction was used to convert ketone VIII (1 g.) to pure **4,5,7,8,9,10-hexahydro-10-methylacephenanthrylene** (XVII) in 68% yield. The hydrocarbon crystallized from acetonitrile or ethanol in square prisms, m.p. 75–76°.

Anal. Calcd. for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.89; H, 8.05.

The 2,4,7-trinitrofluorenone derivative was prepared in benzene and recrystallized from acetonitrile; purple-brown needles, m.p. 165–166°.

Anal. Calcd. for $C_{29}H_{23}N_3O_7$: N, 8.00. Found: N, 7.96.

When 196 mg. of the aforementioned hydrocarbon was heated at 310–325° under nitrogen with 20 mg. of palladium-on-charcoal catalyst for 30 minutes **4,5-dihydro-10-methylacephenanthrylene** (XIX) was obtained in 93% yield (140 mg., m.p. 111–112°, and 39 mg., m.p. 100–108°). Sublimation at 1 mm. gave colorless crystals, m.p. 112–112.5°, which appear as nacreous blades on crystallization from acetonitrile.

Anal. Calcd. for $C_{17}H_{14}$: C, 93.54; H, 6.46. Found: C, 93.38; H, 6.55.

The 2,4,7-trinitrofluorenone derivative separated from benzene as short bright red needles, m.p. 211–212°.

Anal. Calcd. for $C_{29}H_{19}N_3O_7$: N, 8.06. Found: N, 8.15.

Synthesis of 4,5-Dihydro-8,10-dimethylacephenanthrylene (XX).—**8,10-Dimethyl-4,5,7,8,9,10-hexahydroacephenanthrylene** (XVIII) was obtained from ketone XII (1 g.) by heating it to reflux with potassium hydroxide (0.6 g.), 85% hydrazine hydrate (0.43 cc.) and triethylene glycol for 1 hr., and then raising the temperature to 180–195° for 3 hr.[24]; yield 406 mg., m.p. 80–81.5°. Recrystallization of the colorless methanol-soluble portion from ethanol and methanol gave prisms, m.p. 91–91.5° (usually melting first at 85°, then resolidifying).

Anal. Calcd. for $C_{18}H_{20}$: C, 91.47; H, 8.53. Found: C, 91.27; H, 8.73.

Dehydrogenation of XVIII (390 mg.) with palladium-on-charcoal catalyst at 260–310° under nitrogen gave a quantitative yield of nearly colorless **4,5-dihydro-8,10-dimethylacephenanthrylene** (XX), m.p. 97–102°. A portion purified for analysis by vacuum sublimation and crystallization from 100% ethanol, melted at 101–102°; the sample crystallized on cooling, and remelted at 106–106.5°.

Anal. Calcd. for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 93.03; H, 6.91.

The **picrate**, red-orange needles from ethanol, melted at 155.5–156.5°, with previous sintering.

Anal. Calcd. for $C_{24}H_{19}N_3O_7$: N, 9.11. Found: N, 9.15.

Synthesis of 4,5-Dihydro-7,10-dimethylacephenanthrylene (XXI).—A 1.18-g. sample of 10-methyl-4,5,9,10-tetrahydro-7(8)-acephenanthrylenone (VIII) was converted to a gum presumed to be crude 7,10-dimethyl-4,5,7,8,9,10-hexahydro-7-hydroxyacephenanthrylene by reaction[3] with methylmagnesium iodide. The gum was heated in a nitro-

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(23) R. Roger and D. M. Shepherd, *J. Chem. Soc.*, 812 (1954).

(24) Huang-Minlon, THIS JOURNAL, **68**, 2487 (1946).

gen atmosphere with 0.12 g. of 10% palladium-on-charcoal catalyst for 30 minutes at 275–295°. Sublimation *in vacuo* yielded 0.65 g. of semi-crystalline product. From a solution of this material in 15 cc. of ethanol to which was added 13 cc. of saturated ethanolic picric acid, there separated 0.70 g. (31%) of the picrate of the desired hydrocarbon XXI, m.p. 179–181° (with previous softening). Recrystallization from benzene gave dark red needles, m.p. 180–181°.

Anal. Calcd. for $C_{24}H_{19}N_3O_7$: N, 9.11. Found: N, 8.89.

The hydrocarbon was recovered from the picrate by passage through a column of activated alumina, and was purified by sublimation *in vacuo*, followed by recrystallization from acetonitrile and from methanol. **4,5-Dihydro-7,10-dimethylacephenanthrylene** (XXI) took the form of thin colorless blades, m.p. 116.5–117.5°.

Anal. Calcd. for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 92.95; H, 6.80.

LOS ANGELES, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF GENERAL CHEMISTRY OF THE UNIVERSITY OF ROME]

Electronic Transmission through Condensed-ring Systems. II. The Kinetics of Methoxydechlorination of Some 6- and 7-Substituted 1-Aza-4-chloronaphthalenes[1,2]

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RECEIVED SEPTEMBER 24, 1957

The influence of a number of 6- and 7-substituents ranging from dimethylamino to nitro on the bimolecular rate constant for the methoxydechlorination of 4-chloroquinoline has been established. The total range in reactivity at 75° corresponds to a change in rate by a factor of 1.5 × 10⁴. The compounds studied belong to a non-constant entropy of activation series even though the reaction does not suffer from proximity effects by the substituents. There is noted a definite trend of increasing energies of activation with increasing entropies of activation with a maximum scatter in the cases of the nitro and dimethylamino groups. Reactivity is well accounted for by the expected electronic effects of the substituents.

The relative intensity of transmission of the main electronic effects of substituents through fused aromatic rings has been scarcely treated in the literature in contrast with the well known similar effects in benzene derivatives.[3] In the naphthalene system, heteronuclear[4] positions are of several different kinds[5] which are all non-equivalent to the familiar homonuclear positions and may arise from positions relative to α- or β-reacting centers. A good deal of what is known about the effects of heteronuclear substituents on reactivity is due to a paper by Price and Michel,[6] who determined the dissociation and hydrolysis rate constants of a number of substituted β-naphthoic acids and their esters, respectively. Other studies, restricted to the consideration of the nitro and sulfonic groups, have been concerned with the dissociation of naphthols[7,8] and naphthylamines,[9] and with the piperidinodebromination of α- and β-bromonaphthalenes.[10] Data on the effects of aza-substitution on the reactivity of naphthalene derivatives are found in studies on the hydrolysis of quinolinecarboxylic esters[11] and on the piperidinodebromination of bromoquinolines.[12]

Since quinoline is an aza-substituted naphthalene, there are several advantages in considering this system to approach the problem of electronic transmission through fused rings. In the first place, quinoline contains positions (2 and 4) of low electron density from which attached halogens can be displaced easily on nucleophilic attack. Secondly, it contains another reactive center, the basic ring nitrogen, so that nucleophilic rate data can be compared with dissociation constants. Thirdly, reactions at ring carbon or nitrogen are highly susceptible to changes in electron density,[13–17] a condition particularly desirable in a study of the substituent effects at heteronuclear positions[4] from which the electric transmission is expectedly weaker than at *o*-, *m*- and *p*-positions. Finally, the synthesis of many substituted 2- and 4-haloquinolines is at present more accessible than that of nitro- activated naphthalenes.

Studies of the dissociation constants of monosubstituted quinolines have been reported by several authors[18] and those of 6-substituted 4-chloroquinolines by us in Part I.[1] We now wish to report the kinetics of methoxydechlorination[19] of a number of 6- and 7-substituted 4-chloroquinolines.

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[1] Part I, E. Baciocchi and G. Illuminati, *Gazz. chim. ital.*, **87**, 981 (1957).

[2] Presented to the XVIth International Congress of Pure and Applied Chemistry, Paris, July, 1957.

[3] H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

[4] Throughout this work we call heteronuclear positions those at a ring other than the one carrying the reacting center. In the reaction herein dealt with the heteronuclear positions happen to be in the *benzenoid* ring of quinoline.

[5] According to Erdmann's nomenclature for disubstituted naphthalenes, these positions are denoted as *ana*, *epi*, *cata*, *peri*, *amphi* and *pros* (see, for example, V. Grignard, "Traité de Chimie Organique," Vol. XVII (I), Masson et Cie, Paris, 1949, p. 8). In the present paper such a nomenclature has been applied to disubstituted 1-azanaphthalenes.

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[17] J. Miller, *Austr. J. Chem.*, **9**, 61 (1956).

[18] See references in ref. 1.

[19] In this paper we adopt systematic names for nucleophilic substitutions as suggested by J. F. Bunnett, *Chem. Eng. News*, **40**, 4019 (1954).