Experimental

2-Cyano-2-acetoxybicyclo[2,2,1]heptene-5 (III) (Acetate of Dehydronorcamphor Cyanohydrin).—A mixture of 13.0 g. (0.197 mole) of cyclopentadiene (I) and 17.0 g. (0.153 mole) of α-acetoxyacrylonitrile (II) (kindly made available by the B. F. Goodrich Co.) was heated at 100° for 3 hr. The mixture stood overnight at room temperature and was then distilled. There was an 8.5-g. forerun up to 132° (18 mm.) consisting mostly of dicyclopentadiene. The adduct, boiling at 132–137° (18 mm.), was obtained in a yield of 16.8 g. (62%). Redistillation yielded material of b.p. 84–85° (1.5 mm.), $n^{25}\text{D}$ 1.4762. The infrared spectrum in chloroform showed a cyanide band at 6.41 μ and a carbonyl band at 5.76 μ.

Anal. Calcd. for $C_{10}H_{11}NO_2$: C, 67.76; H, 6.26; N, 7.90. Found: C, 67.66; H, 6.16; N, 8.30.

Dehydronorcamphor (IV).—Seven grams of the cyanhydrin acetate III was added to 20 g. of sodium hydroxide in 200 ml. of water containing a few granules of detergent. The mixture was heated under reflux for 2 hr. and then steam distilled. The distillate was saturated with potassium carbonate and extracted with one 25-ml. portion and two 15-ml. portions of ether. After drying and distillation of the ether extract, dehydronorcamphor, b.p. 59.0–59.3° (18 mm.), $n^{25}\text{D}$ 1.4839, was obtained in a yield of 3.51 g. (82%). This material melted at 22–23°. Alder and Rickert reported a melting point of 0–2° for material obtained by oxidation of the alcohol.

Anal. Calcd. for C_7H_8O: C, 77.75; H, 7.45. Found: C, 77.36; H, 7.42.

The semicarbazone melted at 205.8–206.8° after recrystallization from methanol (Alder and Rickert report 207–208°). The infrared spectrum in carbon disulfide showed a double carbonyl peak at 5.76 and 5.80 μ.

Ultraviolet Absorption Spectrum.—The spectrum of dehydronorcamphor from 230 to 330 mμ was determined on a Cary recording spectrometer. The spectrum in ethanol shows a maximum at 300.5 mμ (ϵ 292) and a minimum at 247 mμ (ϵ 6); in 2,2,4-trimethylpentane the maximum is at 308 mμ (ϵ 266), flanked by two subsidiary peaks at 297 and 320 mμ, and the minimum is at 247 mμ (ϵ 6). The presence of the double bond thus results in a shift of the absorption maximum to longer wave lengths by 13.5 mμ and a tenfold increase in the intensity, as compared to norcamphor.[3] This effect is reminiscent of those noted by Braude, Jones, Sondheimer and Toogood.[10] Here, however, any explanation involving hyperconjugation is rendered unlikely by the presence of a bridgehead between the functional groups which are interacting. It is more probable that a direct covalent or electrostatic interaction occurs through space between the 5,6-double bond and the carbonyl group, as suggested to explain the mutual influence of the benzene rings in triptycene upon one another.[11] These spectral effects are probably related to the activation toward solvolysis of the corresponding tosylate by the 5,6-double bond.

Infrared Effects.—In dehydronorcamphor a carbonyl doublet at 5.76 and 5.80 μ takes the place of the single peak at 5.72 observed in 2-norcamphor. Curiously enough, the saturated isomer, 7-norcamphor, has a carbonyl doublet at 5.62 and 5.70 which is replaced by a single peak at 5.62 in the related unsaturated compound, 1,2-dehydro-7-norcamphor.[12]

Acknowledgment.—We are indebted to the B. F. Goodrich Co. for support of this research.

[10] E. A. Braude, E. R. H. Jones, F. Sondheimer and J. T. Toogood, *J. Chem. Soc.*, 607 (1949).

[11] P. D. Bartlett and E. S. Lewis, THIS JOURNAL, **72**, 1007 (1950).

[12] R. B. Woodward and C. J. Norton, *ibid.*, **78**, in press (1956); S. Winstein, M. Shatavsky, C. Norton and R. B. Woodward, *ibid.*, **77**, 4138 (1955).

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE UNIVERSITY]

An Unusual Cyclization in the Naphthalene Series. Synthesis of 1-Ethylanthracene and of 4-Ethylphenanthrene

BY HILLEL BENDAS[1] AND CARL DJERASSI

RECEIVED NOVEMBER 9, 1955

Polyphosphoric acid cyclization of 6-(2-naphthyl)-3-hexanone followed by dehydrogenation yielded 1-ethylanthracene rather than 4-ethylphenanthrene. The latter could be obtained from 4-phenanthrylacetic acid *via* the alcohol, mesylate and iodide.

At an early stage of our examination[2] of the dehydrogenation products of the diterpene cafestol, it was desirable to have available for comparison purposes all of the possible ethylphenanthrenes and the synthesis of the missing isomer—4-ethylphenanthrene—was consequently undertaken.

The most obvious approach involved reaction of 4-keto-1,2,3,4-tetrahydrophenanthrene (I) with ethylmagnesium iodide followed by dehydration and dehydrogenation as has been carried out successfully with the corresponding methyl derivative.[3,4] In the present instance, the Grignard reaction yielded a mixture, which could not be resolved readily, and dehydrogenation afforded chiefly phenanthrene and, in one instance, pyrene (II).[5] While the desired 4-ethylphenanthrene (XI)[5a] was probably formed in this reaction sequence, the difficulty in isolation prompted us to investigate an alternate synthesis.

It was felt that introduction of the ethyl group prior to dehydrogenation would be preferable and consequently γ-2-naphthylbutyric acid (III)[3] was transformed *via* its acid chloride IV to 6-(2-naphthyl)-3-hexanone (V) and cyclized with polyphosphoric acid.[6] The crude cyclization product was directly dehydrogenated with palladized charcoal and the hydrocarbon was characterized by means of the crystalline complexes with picric acid, trinitrobenzene and 2,4,7-trinitrofluorenone[7] as well

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[1] General Foods Corporation Postdoctorate Fellow, 1954–1955.

[2] C. Djerassi, H. Bendas and P. Sengupta, *J. Org. Chem.*, **20**, 1046 (1955).

[3] R. D. Haworth, *J. Chem. Soc.*, 1125 (1932).

[4] W. E. Bachmann and R. O. Edgerton, THIS JOURNAL, **62**, 2219 (1940).

[5] Such cyclodehydrogenations (especially with sulfur) have already been observed by G. Genie, *Ind. Chim. Belg.*, **16**, 576 (1951) (see also D. N. Chatterjee, THIS JOURNAL, **77**, 5131 (1955)). Genie apparently has synthesized 4-ethylphenanthrene without, however, indicating the method or the constants of the compound; his article does not appear to be abstracted in *C. A.*

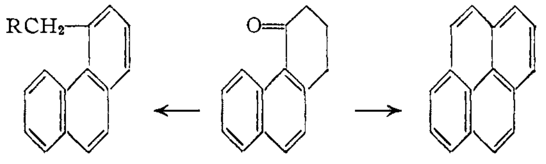
[5a] NOTE ADDED IN PROOF.—Prof. R. H. Martin (University of Brussels) has informed us that this hydrocarbon is described in the Ph.D. thesis of G. Genie (see ref. 5).

[6] *Cf.* J. Koo, THIS JOURNAL, **75**, 1891 (1953), and F. Uhlig, *Angew. Chem.*, **66**, 435 (1954).

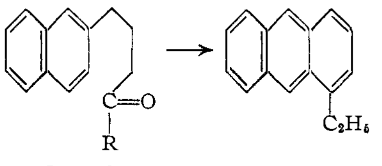
[7] *Cf.* M. Orchin and E. O. Woolfolk, THIS JOURNAL, **68**, 1727 (1946).

as by oxidation to the corresponding quinone. The behavior of this quinone clearly demonstrated that it was not derived from the expected 4-ethylphenanthrene (XI) since it did not form a quinoxaline with *o*-phenylenediamine and its ultraviolet absorption spectrum was essentially superimposable with that of 9,10-anthraquinone. Evidently, cyclization had proceeded by the alternate path to yield the linear product, 1-ethylanthracene (VI), and the physical constants of the picrate and the quinone are in excellent agreement with those recorded for 1-ethylanthracene (VI) derived[8] from 1-acetylanthracene. The only examples in the literature in which linear cyclization of naphthalene derivatives predominated are those in which the reactive 1-position is blocked or where there is a substituent at C-8.[9] While the recorded cases[9] all seem to be limited to substituted γ-2-naphthylbutyric acids, it is clear that the "abnormal" course of the cyclization[10] of the ketone V to 1-ethylanthracene (VI) is a reflection of the same phenomenon, namely, the strong steric interference between substituents in the 4- and 5-positions in the phenanthrene series.[11] It is hoped that a projected study will shed more light on the precise steric requirements of the direction of cyclization of related naphthalene derivatives.

The synthesis of the desired 4-ethylphenanthrene (XI) was finally realized by commencing with 4-phenanthrylacetic acid (VII)[12] in which the potential ethyl group is already present. The acid was reduced with lithium aluminum hydride to the corresponding alcohol VIII which was transformed to the mesylate IX and thence, by sodium iodide in refluxing acetone, to the crystalline iodide X. The selection of the iodide as an intermediate was necessitated by the fact that direct lithium aluminum hydride reduction of the mesylate IX regenerated the alcohol VIII rather than yielding the hydrocarbon XI. Considerable difficulty was encountered in the removal of the iodine atom since reduction with chromous chloride, Raney nickel, palladized charcoal and palladium-on-barium sulfate failed, while treatment with sodium in isopropyl alcohol resulted in simultaneous reduction of the 9,10-double bond. The successful conditions for the conversion of the iodide X to 4-ethylphenanthrene (XI) involved hydrogenation with 2% palladium-on-calcium carbonate catalyst and the oily hydrocarbon was characterized by its crystalline 2,4,7-trinitrofluorenone complex and 9,10-quinone.



VII, R = COOH I II
VIII, R = CH_2OH
IX, R = $CH_2OSO_2CH_3$
X, R = CH_2I
XI, R = CH_3



III, R = OH VI
IV, R = Cl
V, R = C_2H_5

Experimental[13]

6-(2-Naphthyl)-3-hexanone (V).—Pulverized and dried (120°) cadmium chloride (60 g.) was added in portions over a period of 10 min. with stirring to a solution of ethylmagnesium bromide prepared from 10.5 g. of magnesium turnings, 60 g. of ethyl bromide and 200 cc. of anhydrous ether. After cooling in ice, a benzene solution of 50 g. of acid chloride IV (prepared from γ-2-naphthylbutyric acid (III) with thionyl chloride) was added and the mixture was stirred at room temperature for 1 hour and then refluxed for an additional 3 hours. The complex was decomposed with ice-cold hydrochloric acid and the product was extracted with ether, washed with dilute alkali and water, dried and evaporated. The crude ketone (48 g.) was purified by treatment with an equal weight of Girard reagent T and the ketonic fraction was crystallized from ethanol to yield 32 g. of the ketone V, m.p. 47–49°.

Anal. Calcd. for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 84.53; H, 8.24.

The semicarbazone was crystallized from ethanol, whereupon it exhibited m.p. 152–154°.

Anal. Calcd. for $C_{17}H_{21}N_3O$: C, 72.05; H, 7.47. Found: C, 71.70; H, 7.54.

1-Ethylanthracene (VI).—A mixture of 16 g. of 6-(2-naphthyl)-3-hexanone (V) and 50 g. of polyphosphoric acid was heated on the steam-bath for 1.5 hours, diluted with water and extracted with ether. The residue, obtained after evaporation of the washed and dried solution, was treated with 16 g. of Girard reagent T yielding 9.2 g. of non-ketonic material, which was heated for 30 minutes with 2 g. of 30% palladized charcoal at 300°. The mixture was extracted with acetone, giving 8.6 g. of crude hydrocarbon, which was treated with 8 g. of trinitrobenzene in ethanol solution. The resulting complex (10 g.) was filtered and a small sample was recrystallized from ethanol as reddish-orange crystals, m.p. 98–99°.

Anal. Calcd. for $C_{22}H_{17}N_3O_6$: C, 63.00; H, 4.09. Found: C, 63.37; H, 4.19.

A benzene solution of the trinitrobenzene complex was passed through 500 g. of activated alumina and the 1-ethylanthracene (VI), eluted with benzene, was distilled *in vacuo*; b.p. 168–172° at 1.5 mm., yield 4.4 g.; λ_{max}^{EtOH} 222 (log ε 4.44), 253 (5.28), 276 (3.97), 285 (3.80), 295 (3.90), 310 (3.34), 330 (3.62), 340 (3.88) and 365 mμ (4.06); λ_{min}^{EtOH} 227 (4.29), 272 (3.95), 283 (3.75), 290 (3.70), 307 (3.31), 315 (3 32), 330 (3.57) and 347 mμ (3.71).

Anal. Calcd. for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 93.00; H, 6.98.

The red picrate was crystallized from ethanol, m.p. 126–127° (lit.[8] m.p. 126–127°).

Anal. Calcd. for $C_{22}H_{17}N_3O_7$: C, 60.69; H, 3.94. Found: C, 60.80; H, 4.00

The reddish-brown 2,4,7-trinitrofluorenone complex was recrystallized from ethanol solution, m.p. 177–178°.

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(8) H. Waldmann and E. Marmorstein, *Ber.*, **70**, 106 (1937).

(9) W. S. Johnson, *Org. React.*, **2**, 114 (1944).

(10) The "abnormal" linear cyclization of 4-(2-naphthylimino)-2-pentanone and of related anils (W. S. Johnson and F. J. Mathews, THIS JOURNAL, **66**, 210 (1944)) for which an electronic effect has been proposed (W. S. Johnson, E. Woroch and F. J. Mathews, *ibid.*, **69**, 566 (1947)) may actually be due to the same type of steric interference operating in the above described linear cyclization of 6-(2-naphthyl)-3-hexanone (V).

(11) *Cf.* M. S. Newman, *ibid.*, **62**, 2295 (1940), and later papers.

(12) M. S. Newman, *J. Org. Chem.*, **16**, 870 (1951). We are indebted to Prof. Newman for helpful suggestions in connection with this synthesis.

(13) All melting points were determined on the Kofler block. We are indebted to Mrs. Dolores Phillips for the ultraviolet absorption spectra measured with an automatically recording Warren Spectracord and to Spang Microanalytical Laboratory (Plymouth, Michigan) for the microanalyses.

Anal. Calcd. for $C_{29}H_{19}N_3O_7$: C, 66.79; H, 3.67; N, 8.06. Found: C, 66.82; H, 3.57; N, 8.12.

When 1.35 g. of 1-ethylanthracene (VI) was oxidized in boiling acetic acid solution for 3–5 minutes with 3 g. of chromium trioxide, there was obtained 1.05 g. of 1-ethyl-9,10-anthraquinone, m.p. 81–83°. Two recrystallizations from ethanol led to the analytical sample as yellow crystals, m.p. 93–94° (lit.[8] m.p. 96°); λ_{max}^{EtOH} 253 (log ϵ 4.69), 273 (4.22) and 333 mμ (3.82); λ_{min}^{EtOH} 268 (4.22) and 292 mμ (3.40). 9,10-Anthraquinone was measured at the same time and exhibited λ_{max}^{EtOH} 252 (4.75), 272 (4.26) and 325 mμ (3.80); λ_{min}^{EtOH} 267 (4.23) and 289 mμ (3.36).

Anal. Calcd. for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12. Found: C, 81.65; H, 5.30.

4-Ethylphenanthrene (XI).—4-Phenanthrylacetic acid (VII)[12] (2.4 g.) was reduced at room temperature in ether solution with 3 g. of lithium aluminum hydride to give the corresponding **alcohol VIII** in nearly quantitative yield; m.p. 76–78° after recrystallization from benzene–hexane.

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.78; H, 6.49.

The above alcohol VIII (2.2 g.) in pyridine solution was left overnight in the refrigerator with 1 cc. of methanesulfonyl chloride. After processing in the usual way and crystallizing from ether, there was obtained 1.5 g. of the **mesylate IX**, m.p. 83–84°.

Anal. Calcd. for $C_{17}H_{16}O_3S$: C, 67.99; H, 5.37. Found: C, 68.13; H, 5.29.

The mesylate was transformed to the alcohol VIII when it was reduced with lithium aluminum hydride in dioxane solution for 12 hours by the soxhlet technique.

The conversion to the **iodide X** was accomplished by refluxing 1.4 g. of the mesylate IX with 1.5 g. of sodium iodide in 150 cc. of acetone for 14 hours. The precipitate was filtered, the filtrate was evaporated to dryness and the residue was taken up in ether and washed well with dilute sodium thiosulfate solution, dilute sodium hydroxide, water, and then dried and evaporated. The crude iodide (1.0 g., m.p. 46–50°) was recrystallized twice from ethanol whereupon it exhibited m.p. 50–51°.

Anal. Calcd. for $C_{16}H_{13}I$: C, 57.85; H, 3.94; I, 38.21. Found: C, 58.31; H, 4.14; I, 37.75.

Deiodination with chromous chloride, 5% palladium-on-barium sulfate, 5% palladized charcoal or Raney nickel failed, the compound being recovered unchanged. Treatment of 500 mg. of the iodide in 50 cc. of boiling isopropyl alcohol solution with 2.3 g. of sodium yielded 270 mg. of a halogen-free oil, but its ultraviolet absorption spectrum was typical of a 9,10-dihydrophenanthrene and consequently no further work was done with this product.

Deiodination was finally effected by hydrogenating 660 mg. of the iodide X in 60 cc. of methanol with 2 g. of 2% palladium-on-calcium carbonate catalyst for 24 hours, the system being swept out with fresh hydrogen at 5-hour intervals. The catalyst was filtered, the filtrate was diluted with water and the product was isolated with ether and washed well with thiosulfate solution and water, dried and evaporated. A 300-mg. portion of the halogen-free oil, obtained in nearly quantitative yield, was treated in ethanol solution with 2,4,7-trinitrofluorenone and the orange-colored complex (200 mg.) was filtered and recrystallized several times from the same solvent, whereupon it showed m.p. 145–147°.

Anal. Calcd. for $C_{29}H_{19}N_3O_7$: C, 66 79; H, 3.67; N, 8.06. Found: C, 66.96; H, 3.77; N, 8.04.

A 200-mg. sample of the 2,4,7-trinitrofluorenone complex was decomposed by passage of a benzene solution over 25 g. of alumina and the hydrocarbon was distilled at a bath temperature of *ca.* 140° and 0.1 mm.; λ_{max}^{EtOH} 252 mμ (log ϵ 4.83), 276 (4.04), 288 (4.02), 298 (4.07), 318 (2.82), 334 (2.99) and 350 mμ (2.65); λ_{min}^{EtOH} 233 (4.42), 274 (4.03), 281 (3.95), 292 (3.87), 314 (2.70), 326 (2.62) and 346 mμ (2.36).

Anal. Calcd. for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 92.88; H, 7.13.

4-Ethyl-9,10-phenanthrenequinone was prepared by chromium trioxide oxidation as described for VI and was purified by sublimation; yellow needles, m.p. 127–128°.

Anal. Calcd. for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12. Found: C, 81.29; H, 5.34.

Attempted Synthesis of 4-Ethylphenanthrene from 4-Keto-1,2,3,4-tetrahydrophenanthrene (I).—A solution of 10 g. of the ketone I[3,14] in benzene was stirred for 36 hours at 0° with a Grignard solution prepared from 5 g. of magnesium turnings, 16 g. of ethyl iodide and 200 cc. of ether. Decomposition with ammonium chloride, extraction with ether and slow crystallization of the residue from benzene–hexane yielded 0.6 g. of crystals, m.p. 142–145°, which judging from the analysis (Calcd. for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 85.50; H, 7.53) represented chiefly the desired ethylcarbinol.[15] However, dehydrogenation of this crystalline compound or of the oily mother liquor with 30% palladized charcoal at 320° for 30 minutes yielded phenanthrene as the only recognizable product.

In a second experiment, the crude Grignard reaction product from 20 g. of I was subjected to a Girard separation with 20 g. of Girard reagent T, 20 cc. of acetic acid and 200 cc. of absolute ethanol and the non-ketonic fraction was distilled at 135–140° and 0.5 mm. The oily distillate (10.2 g.), probably consisting of a mixture of 4-ethyl-1,2-dihydrophenanthrene and some of the ethylcarbinol (*Anal.* Calcd. for $C_{16}H_{16}$: C, 92.26; H, 7.74. Calcd. for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 89.12; H, 8.13), was dehydrogenated with 30% palladized charcoal by heating for 1 hour at 280° and an additional hour at 300°. Approximately 5% of **pyrene (II)** was isolated, m.p. 151–153°, undepressed upon admixture with an authentic sample kindly furnished by Prof. L. F. Fieser (Harvard University).

Anal. Calcd. for $C_{16}H_{10}$: C, 95.02; H, 4.98. Found: C, 95.46; H, 5.01.

The oily mother liquors gave crystalline adducts with trinitrobenzene and 2,4,7-trinitrofluorenone which had a wide melting point range and which were not further investigated.

DETROIT, MICHIGAN

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(14) W. E. Bachmann and G. D. Cortes, THIS JOURNAL, **65**, 1329 (1943).

(15) In order to preclude that this was the simple reduction product, 1-hydroxy-1,2,3,4-tetrahydrophenanthrene, an authentic sample of the latter was prepared by sodium borohydride reduction of I and found to melt at 130–132° after recrystallization from benzene (*Anal.* Calcd. for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.52; H, 7.12).