and 1,1-diphenylethylene oxide gave diphenylbenzylcarbinol and its dehydration product. These results have been interpreted in terms of a reaction mechanism for the opening of the 1,2-epoxide ring with organolithium compounds.

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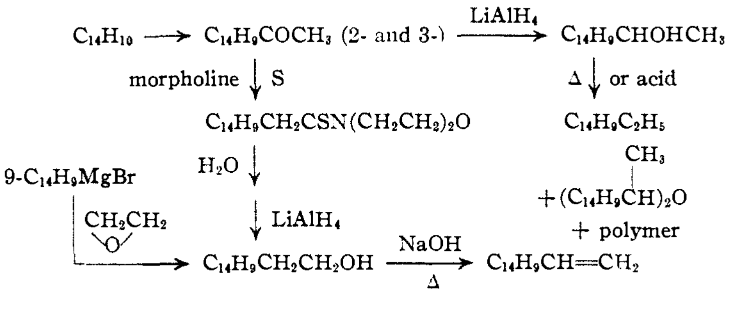
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

2-, 3- and 9-Vinylphenanthrenes[1a]

BY CHARLES C. PRICE AND BENJAMIN D. HALPERN[1b]

The synthesis of 2-, 3 and 9-vinylphenanthrenes has been accomplished most successfully through alkaline dehydration of the corresponding β-phenanthrylethanols. The β-(2- and β-(3-phenanthryl)-ethanols were prepared by Willgerodt transformation on the 2- and 3-acetyl derivatives, followed by hydrolysis of the thioamides and lithium hydride reduction of the corresponding phenanthrylacetic acids. Physical properties, including ultraviolet absorption data, are reported for many of the intermediates, products and their derivatives.

In order to extend the knowledge of arylethylenes, of potential interest as monomers in vinyl polymerization, the preparation and characterization of three isomeric vinylphenanthrenes have been investigated. Attempts to dehydrate the α-phenanthrylethanols from reduction of 2- and 3-acetylphenanthrene by thermal or catalytic procedures were unpromising. Apparently the desired vinyl compounds were too sensitive to polymerization. From these experiments some ethylphenanthrene and some ether of the reactant alcohol were isolated. 2- and 3-acetylphenanthrene were successfully converted to the vinyl compounds through Willgerodt transformation, hydrolysis to the phenanthrylacetic acids, lithium aluminum hydride reduction and dehydration of the β-phenanthrylethanols over alkali. β-(9-Phenanthryl)-ethanol was prepared by reaction of the Grignard reagent of 9-bromophenanthrene with ethylene oxide and was also successfully dehydrated over alkali. Most of the compounds prepared have been characterized as their complex with 2,4,7-trinitrofluorenone (T.N.F.).[2]



Results of the investigation of the copolymerization properties of these three arylethylenes will be reported elsewhere.

Incidental to the work, tests were made on the plant growth activity of the intermediate phenanthrylacetic acids. These acids were apparently less effective than β-indolylacetic acid, with the 3-isomer slightly the more effective.[3]

Experimental[4]

2- and 3-Acetylphenanthrenes.—Especially purified phenanthrene (Reilly) was recrystallized once from ethanol, m.p. 98–98.5°. Color reaction with hot and cold concentrated sulfuric acid indicated a high degree of purity.[5] Acetylation, separation and purification were carried out according to Mosettig and van de Kamp[6] to yield 19% of 2-acetylphenanthrene, m.p. 144° (lit. 143°, 15%) and 66.5% of 3-acetylphenanthrene, m.p. 71° (lit. 72°, 63.5%).

2,4,7-Trinitrofluorenone complexes[7] were prepared by mixing hot equimolar benzene solutions of the reagent and the reactant. The yellow to orange precipitates were recrystallized from ethanol. The melting points and analyses are summarized in Table I.

α-2- and α-3-(Phenanthryl)-ethanols.—Reductions of the acetylphenanthrenes were found to proceed more smoothly and in better yield with lithium aluminum hydride than with aluminum isopropoxide. Using essentially the procedure of Nystrom and Brown,[8] 75 g. of 2-acetylphenanthrene (m.p. 135–139°, 0.34 mole) was treated with 6.0 g. of lithium aluminum hydride in 800 ml. of ether. Washing and evaporation left 72 g. (95%) of the carbinol. After precipitation from benzene by Skellysolve "F" it melted at 128.5–130.8° (lit., 131–131.5°,[9] 134–135°[10]). Similar reduction of 140 g. of 3-acetylphenanthrene (m.p. 68–69°) with 19 g. of lithium aluminum hydride in 400 ml. of ether yielded 126 g. (96.5%) of the carbinol, m.p. 76–78° (lit. 79–81°,[11] 83–83.5°[10]).

The acetate of α-2-(phenanthryl)-ethanol was prepared from 20 g. of the alcohol in 200 ml. of pyridine by heating with 80 g. of acetic anhydride. The crude white product, 23 g., m.p. 61–63°, was recrystallized from ethanol to yield 17 g., m.p. 66.8–67.6°.

Anal. Calcd. for $C_{18}H_{16}O_2$: C, 81.78; H, 6.10. Found: C, 81.76; H, 6.45.

The acetate of the 3-isomer was obtained as a viscous oil, b.p. 171–172° (0.03 mm.). Reaction with bromine (bromine no.,[12] 3.4; calcd. for vinylphenanthrene, 78.8), with permanganate, and saponification equivalent (calcd., 263; found 276) indicated contamination with approximately 5% of the vinylphenanthrene. The **picrate** prepared from this oil could be successfully crystallized from ethanol saturated with picric acid as dense clusters of yellow needles, m.p. 82.4–85.6°. The melting range and analysis indicate some contamination with excess picric acid.

Anal. Calcd. for $C_{24}H_{19}O_9N_3$: C, 58.42; H, 3.88; N, 8.51. Found: C, 57.23; H, 3.81; N, 8.82.

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(1) (a) Abstracted from a portion of the Ph.D. thesis submitted to the Graduate School by Benjamin D. Halpern. (b) General Tire and Rubber Co. Fellow, 1947–1948; Socony–Vacuum Oil Co. Fellow, 1948–1949.

(2) Available from Dajac Laboratories, 3430 W. Henderson St., Chicago, Ill.

(3) We are indebted to Professor Albert D. DeLisle, Department of Biology, University of Notre Dame, for this information.

(4) Analyses by Micro Tech Laboratories, Skokie, Illinois.

(5) Price, THIS JOURNAL, **60**, 2839 (1938).

(6) Mosettig and van de Kamp, *ibid.*, **52**, 3704 (1930).

(7) Orchin and Woolfolk, *ibid.*, **68**, 1727 (1946).

(8) Nystrom and Brown, *ibid.*, **69**, 1197 (1947).

(9) Bachmann and Struve, *J. Org. Chem.*, **5**, 420 (1940).

(10) Mosettig and van de Kamp, THIS JOURNAL, **55**, 3442 (1933).

(11) Bachmann and Chemerda, *J. Org. Chem.*, **6**, 36 (1941).

(12) Uhrig and Levin, *Ind. Eng. Chem. Anal. Ed.*, **13**, 90 (1941).

TABLE I

PROPERTIES OF 2,4,7-TRINITROFLUORENONE COMPLEXES

Phenanthrene derivative	M.p., °C.	Crystal form	Analyses, % Calcd. C	H	N	Found C	H	N
2-Acetyl	155	Yellow	65.05	3.20	7.85	65.64	3.02	7.54
3-Acetyl	185	Yellow	65.05	3.20	7.85	65.05	3.17	7.90
2-(α-Hydroxyethyl)	154	Orange-yellow	[a]	..	..	...	..	..
3-(α-Hydroxyethyl)	162	Orange	[a]	..	..	...	..	..
3-(α-Acetoxyethyl)	165.9–167.8	Orange buttons	64.25	3.65	7.25	64.31	3.64	7.30
2-(β-Hydroxyethyl)	154.4–154.7	Yellow	64.80	3.54	7.82	64.75	3.43	7.68
2-Vinyl	180.9–181.2	Golden yellow	67.05	3.30	8.09	66.88	3.40	8.11
3-Vinyl	177.8–178.8	Orange needles	67.05	3.30	8.09	67.30	3.44	7.86
9-Vinyl	169.9–170.5	Orange plates	67.05	3.30	8.09	67.32	3.40	8.14
α,α'-Bis-(3-Ph)-ethyl ether	209.6–210.2	Orange	65.91	3.41	7.96[b]	66.60	3.36	7.82

[a] These complexes decomposed on attempted recrystallization from ethanol. [b] Calculated for two moles of T. N. F. per mole of ether.

TABLE II

PHYSICAL PROPERTIES AND ANALYTICAL DATA OF PHENANTHRENE DERIVATIVES

Phenanthrene derivative	M.p., °C. cor.	Yield, %	Crystal solvent	Crystal form	Molecular formula	Analyses, % Calcd.	Found	Calcd.	Found
2-Acetothiomorpholide	157[a]	98	Abs. EtOH	Pale yellow	$C_{20}H_{19}NOS$	C, 74.73 N, 4.36	73.83 4.41	H, 5.96 S, 9.96	5.94 10.75
3-Acetothiomorpholide	Oil	98	...	....	$C_{20}H_{19}NOS$	N, 4.36	4.50	S, 9.96	9.91
2-Acetic ester, ethyl	52.8–53.7	..	EtOH	Slender needles	$C_{18}H_{16}O_2$	C, 81.79	81.82	H, 6.10	6.20
β-2-Ethanol	115–116	86	MeOH	....	$C_{16}H_{14}O$	C, 86.44	85.50	H, 6.35	6.06
β-2-Ethanol, dinitrobenzoate	219–223[b]	..	Abs. EtOH	....	$C_{23}H_{16}H_2O$	C, 66.35 N, 6.73	66.58 6.30	H, 3.87	3.86
β-3-Ethanol	55.6–57.0	86	Cyclohexane	....	$C_{16}H_{14}O$	C, 86.44	85.68	H, 6.35	6.19
β-3-Ethanol, dinitrobenzoate	272–273	..	C_6H_6	....	$C_{23}H_{16}N_2O_6$	C, 66.35	66.27	H, 3.87	3.93
β-3-Ethanol, acetate	45.3–45.4	..	Aq. EtOH	Plates	$C_{18}H_{16}O_2$	C, 81.79	81.40	H, 6.10	5.97
2-Vinyl	116.5–118	*ca.* 40	MeOH	Plates	$C_{16}H_{12}$	C, 94.08	94.10	H, 5.92	6.14
2-Vinyl, picrate	90.–92.2	..	EtOH	Long, orange needles	$C_{22}H_{15}N_3O_7$	C, 60.97 N, 9.69	61.20 10.35	H, 3.49	3.44
2-Vinyl, dibromide[c]	148.2–148.9	..	MeOH	Long needles	$C_{16}H_{12}Br_2$	C, 52.78 Br, 43.90	53.01 43.86	H, 3.32	3.51
3-Vinyl	58.2–59.4	59	EtOH	Hexagonal plates	$C_{16}H_{12}$	C, 94.08	93.77	H, 5.92	5.93
3-Vinyl, picrate	105.8–107.8	..	EtOH	....	$C_{22}H_{15}N_3O_7$	C, 60.97 N, 9.69	61.24 9.57	H, 3.49	3.50
3-Vinyl, dibromide[c]	133.6–135.6	..	$CHCl_3$–Skellysolve "F"	Silky needles	$C_{16}H_{12}Br_2$	C, 52.78	52.86	H, 3.32	3.50
3-Ethylene glycol[d]	136.8–137.8	10	Skellysolve "L"	....	$C_{16}H_{14}O_2$	C, 80.65	80.88	H, 5.92	6.10
β-6-Ethanol, acetate	74.2–74.9	..	EtOH	Needles	$C_{18}H_{16}O_2$	C, 81.79	81.46	H, 6.10	6.03
9-Vinyl	36.4–37.8[e]	73	EtOH	Long needles	$C_{16}H_{12}$	C, 94.08	92.21	H, 5.92	6.34
9-Vinyl, picrate[f]	132.8–133.7	..	EtOH	Orange needles	$C_{22}H_{15}N_3O_7$	C, 60.97 N, 9.69	60.50 10.04	H, 3.49	3.55
9-Vinyl, dibromide[c]	125.2–125.8	..	$CHCl_3$	Silky needles	$C_{16}H_{12}Br_2$	C, 52.78 Br, 43.90	52.68 43.60	H, 3.32	3.85

[a] Schwenk and Block[13] have reported this substance as an oil. [b] Phase change at 200–202°. [c] The vinyl dibromides were prepared by titrating vinyl compound in chloroform with bromine in chloroform to pale yellow end-point. The products were precipitated with Skellysolve "F." [d] By oxidation of 1 g. of 3-vinyl with 1 g. of potassium permanganate in 50 ml. of aqueous methanol. [e] Bergmann and Bergmann (THIS JOURNAL, **59**, 1443 (1937)) report this product as an oil, b.p. 150–160° (1 mm.), C, 92.10; H, 6.1. [f] Reaction of the vinyl compound in ethanol with bromine in acetic acid produced a substance, recrystallized from methanol as needle clusters, whose analysis indicated it to be the bromovinyl compound, m.p. 75–77.2°. *Anal.* Calcd. for $C_{16}H_{11}Br$: Br, 28.22. Found: Br, 29.84.

Treatment of α-(2-phenanthryl)-ethanol with pyridine and thionyl chloride produced a material which repeatedly crystallized from ethanol as plates, m.p. 98–102°. The compound gave positive tests for unsaturation and for active chlorine (silver nitrate). These observations coupled with the analytical data suggest that this material was a molecular compound consisting of two moles of vinylphenanthrene and one of the chloroethyl derivative.

Anal. Calcd. for $2C_{16}H_{12}\cdot C_{16}H_{13}Cl$: C, 88.79; H, 5.75; Cl, 5.46. Found: C, 88.85; H, 5.79; Cl, 5.36.

Attempted Tschugaeff dehydration of this alcohol through pyrolysis of the xanthate gave a poor yield of material crystallizing from methanol as short needles, m.p. 60–78°, analyzing for **methylmercaptoethylphenanthrene.**

Anal. Calcd. for $C_{17}H_{16}S$: C, 80.90; H, 6.39; S, 12.70. Found: C, 80.03; H, 6.20; S, 12.70.

α-(2-Phenanthryl)-ethanol was resistant to dehydration, distilling unchanged from a flash chamber at 375° (1 mm.). Dehydration with potassium acid sulfate at 175° under 0.08–0.10 mm. pressure left most of the organic material as a non-volatile polymer.

When α-(3-phenanthryl)-ethanol was passed over silica gel beads at 425° a small amount of yellow oil was collected. The melting point of the T.N.F. derivative, m.p. 158–159°, agreed with that for 3-ethylphenanthrene. Thermal treatment at 375° gave a distillate which gave the following melting points on successive recrystallizations from benzene: 109.5–110°, 112–113°, 122–123°. Analysis and melting point of the T.N.F. derivative indicate it to be a crystalline modification of the starting alcohol.

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.44; H, 6.35. Found: C, 86.26; H, 6.35.

The T.N.F. derivative melted at 162°.

Anal. Calcd. for $C_{16}H_{14}O\cdot C_{13}H_5N_3O_7$: C, 64.80; H, 3.54. Found: C, 65.22; H, 3.67.

From similar thermal experiments at a higher temperature (400°) the oily distillate had $n^{20}D$ 1.6818, d^{20} 1.1068. By bromine titration it contained 16.5% 3-vinylphenanthrene, the presence of which was confirmed by isolation of its dibromide, m.p. 130.6-131.8°. When the oil was dissolved in ethanol, 5% separated, hexagonal plates from *n*-hexane, m.p. 195.5-196°. Analysis indicated it to be α,α'-bis-(3-phenanthryl)-ethyl ether.

Anal. Calcd. for $C_{32}H_{26}O$: C, 90.14; H, 6.10. Found: C, 90.13; H, 6.21.

2-(and 3)-Phenanthrylthioacetomorpholides.—The Schwenk and Bloch[13] modification of the Willgerodt reaction was improved by using the ratio of reactants of King and MacMillan.[14] Boiling 100 g. of 2-acetylphenanthrene with 36.5 g. of sulfur in 82 g. of morpholine yielded 144 g. of a brick red powder.

A similar reaction starting with 22 g. of 3-acetylphenanthrene produced 32 g. of a very viscous, taffy-like material. It was undecomposed but undistillable at 260° under 0.05 mm. After reprecipitation from ethanol by water, the oil analyzed properly.

2-(and 3)-Phenanthrylacetic acids were obtained most satisfactorily by hydrolysis of the thiomorpholides in ethanolic potassium hydroxide. The 2-isomer gave the acid in 94% yield; plates, m.p. 194.3-194.9°.[15]

The acid was converted to its **ethyl ester; methyl ester,** needle clusters from alcohol, m.p. 77-78.2° (lit.[10] 78-78.5°).

The 3-phenanthrylacetic acid was prepared in 87% overall yield from 3-acetylphenanthrene; plates from alcohol, m.p. 176.8-178.3° (lit.[15a] 177-177.5°). The acid was usually accompanied by 5-10% of alkali-insoluble material which proved to be 3-phenanthrylacetomorpholide; white plates from absolute ethanol, m.p. 139.2-139.9°.

Anal. Calcd. for $C_{20}H_{19}NO_2$: C, 78.62; H, 6.27; N, 4.58. Found: C, 78.58; H, 6.34; N, 4.67.

β-(2-Phenanthryl)-ethanol was prepared from 137 g. of crude 2-phenanthrylacetic acid by reduction with 40 g. of lithium aluminum hydride in 2.5 l. of anhydrous ether.

2-Vinylphenanthrene was prepared by immersing in a Woods metal bath at 200° an intimate mixture of 41 g. of β-(2-phenanthryl)-ethanol with 41 g. of solid sodium hydroxide contained in a 500-ml. stainless steel, standard-taper flask equipped with a distilling head and condenser and maintained at 0.1 mm. pressure. A total of 33 g. of distillate was recovered up to 280°. Recrystallization from methanol gave 16.7 g., m.p. 95-103°, 76% pure according to bromine number, and a second fraction, 4 g., m.p. 79-88°, 50% pure.

When the treatment was carried out in the presence of air, polymer infusible at 250° was formed. In one experiment fractional crystallization yielded a small amount of 2-ethylphenanthrene, m.p. 57-61° (lit.[10] 67-68°), picrate, m.p. 94-97° (lit.[10] 95.5-96°).

3-Vinylphenanthrene was prepared by dropping 70 g. of crude β-(3-phenanthryl)-ethanol on 50 g. of solid sodium hydroxide maintained at 370° and 1 mm. pressure in a 500-ml. standard-taper copper flask.[16] Recrystallization of the 50 g. of light yellow distillate (m.p. 35-45°) from methanol gave 37.9 g. (59%) of 3-vinylphenanthrene, m.p. 53.7-57.2° (95% pure by bromine titration).

β-(9-Phenanthryl)-ethanol was prepared by reaction of 9-phenanthrenemagnesium bromide with ethylene oxide.[17] Recrystallization from cyclohexane gave a 75% yield of white needles, m.p. 86.5-88° (lit.[17] 92°).

9-Vinylphenanthrene was prepared by dehydration of the alcohol above in the same way as the 2-isomer; yield 73%, b.p. 194-197° (5-7 mm.). On long standing, the water-white distillate crystallized.

Tetrahydrotriphenylenedicarboxylic acid anhydride was prepared by reaction of 9-vinylphenanthrene with maleic anhydride in refluxing xylene. Recrystallization from dioxane, of the crystals which separated from the xylene on cooling gave long, white needles, m.p. 216-222°.[18]

Anal. Calcd. for $C_{20}H_{14}O_3$: C, 79.46; H, 4.67. Found: C, 78.82; H, 4.63.

Similar treatment of the 2- and 3-vinylphenanthrenes with maleic anhydride produced granular solids unmelted at 320°. These materials were insoluble in alkali and the usual organic solvents. The properties and analysis of the material from the 3-isomer suggest they are the 1:1 **copolymers.**

Anal. Calcd. for $(C_{16}H_{12}\cdot C_4H_2O_3)_n$: C, 79.46; H, 4.67. Found: C, 78.48; H, 4.75.

Ultraviolet absorption spectra were determined by a Beckman quartz spectrophotometer using chloroform as a solvent. The results are summarized in Table III.

TABLE III

MOLAR EXTINCTION COEFFICIENTS FOR MAXIMA IN ULTRAVIOLET ABSORPTION

Isomer	Wave length, mμ	ε, l./mole-cm.
A. β-Phenanthrylethanols		
2-	330	204
3-	350	378
3-	300	20,300
9-	350	286
9-	334	337
9-	300	9,900
B. Vinylphenanthrenes		
2	362.5	350
2-	345	440
2-	330	360
2-	295	24,800
2-	270	40,600
3-	360	432
3-	342	655
3-	315	21,700
3-	302	21,600
9-	300	12,160

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[13] Schwenk and Bloch, THIS JOURNAL, **64**, 3051 (1942).

[14] King and MacMillan, *ibid.*, **68**, 2335 (1946).

[15] (a) Mosettig and van de Kamp, *ibid.*, **55**, 2995 (1933)) report this acid as needles, m.p. 183.5-184.5°. (b) Wilds (*ibid.*, **64**, 1428 (1942)) reports it as plates, m.p. 194.5-195.5°.

[16] When this procedure was applied to β-(2-phenanthryl)-ethanol, the alcohol distilled over unchanged.

[17] Bergmann and Blum-Bergmann, THIS JOURNAL, **58**, 1678 (1936).

[18] Bergmann and Bergmann, *ibid.*, **59**, 1443 (1937), report a m.p. of 218-220° but their analysis indicated their product to be the acid.