

recrystallizations from methanol, 0.22 g of product was recovered: $[\alpha]_D^{25} -21.7^\circ$ (*c* 1.2, acetone); mp $75-76^\circ$ [lit.¹⁶ mp $76-77^\circ$; $[\alpha]_D +6.67^\circ$ (*c* 14.8, acetone)]. The infrared spectrum did not change with recrystallization.

A second reaction performed under very similar conditions gave (-)-1,1,2-triphenylpropane, $[\alpha]_D -3.38^\circ$ (*c* 27.8, acetone), in 93% yield from (-)- α -phenylethyl chloride, $[\alpha]_D^{24} -15.0^\circ$ (neat, *l* = 1 dm).

Registry No.—(+)-2-Bromobutane, 5787-32-6; (-)-2-bromooctane, 5798-55-2; (+)-2-bromooctane, 1191-24-8; (-)-2-chlorooctane, 18651-57-5; (+)- α -phenylethyl chloride, 1459-15-0; (-)- α -phenylethyl chloride, 3756-41-0; benzyl lithium, 766-04-1; allyllithium, 3052-45-7; benzhydryllithium, 881-42-5.

Metal-Ammonia Reduction. VII. Stereospecific Reduction in the Phenanthrene Series^{1,2}

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Phenanthrene and its 9-alkyl- and 9,10-dialkyl derivatives are efficiently reduced in the 9,10 position by lithium in ammonia in the presence of colloidal iron. 9,10-Dimethyl- and 9,10-diethylphenanthrene undergo stereospecific *cis* reduction under these conditions. The corresponding *trans* diastereomers required for comparison by variable-temperature nmr were synthesized *via* alkylation of the corresponding 9-alkyl-10-lithio-9,10-dihydrophenanthrenes. The unstable second-stage reduction product of phenanthrene was assigned the 2,4a,9,10-tetrahydrophenanthrene structure on the basis of nmr and uv data, and comparison with its 4a-methyl homolog obtained through reductive methylation of phenanthrene. Stereospecific *cis* reduction and *trans* alkylation are explicable in terms of the conformational properties of the respective monoanionic intermediates and preferential axial attack during final protonation and alkylation, respectively.

Efficient single-stage reduction of a series of representative polycyclic aromatic hydrocarbons (anthracene, naphthalene, benz[*a*]anthracene, dibenz[*a,h*]anthracene, 3-methylcholanthrene, and pyrene) by lithium dissolved in liquid ammonia was described in parts I–IV of this series.³ The structures of the dihydro products accorded, in general, with predictions⁴ based upon molecular orbital calculations of the positions of highest electron density in the anionic intermediates. Also, stepwise reduction (of anthracene and benz[*a*]anthracene^{3b}) provided products whose structures at each stage were in accord with qualitative prediction of relative anionic stabilities. The steric course of reduction also proved highly specific;^{3a} 9,10-dialkylanthracene and 7,12-dimethylbenz[*a*]anthracene furnished the corresponding *trans*-dialkyldihydro derivatives exclusively.⁵

The present paper reports detailed investigation of reduction in the phenanthrene series. Evidence is presented concerning the stereochemistry of reduction of 9,10-dialkylphenanthrene, the structures of secondary products, and the effects of reaction variables on the course of reaction.

Previous investigations have been confined to phenanthrene itself. Hückel and Bretschneider⁶ reported treatment of phenanthrene in liquid ammonia with 2 g-atoms of sodium to provide small quantities of 9,10-dihydrophenanthrene; 4 equiv of the metal gave a mixture believed to contain 1,2,3,4-tetrahydrophenanthrene. Analogous reduction in the presence of alcohol

furnished, according to Mejer,⁷ 1,2,3,4,4a 9,10,10a-octahydrophenanthrene as the sole product.

Results

Phenanthrene, in accord with theoretical prediction,⁴ underwent preferential lithium-ammonia reduction at the 9,10 position.^{3a} However, under conditions previously demonstrated to provide efficient transformation of acene hydrocarbons to dihydro derivatives,³ reduction of phenanthrene and 9-methylphenanthrene was incomplete and accompanied by secondary products (Table I, experiments 1, 2, and 9).

A brief investigation of reaction conditions led to an improved procedure which provided 9,10-dihydro derivatives of phenanthrene (**1a**), 9-alkylphenanthrene (**1b** and **1c**), and 9,10-dialkylphenanthrene (**1d** and **1e**) (Chart I) with yields generally of 70–80% (Table I). The beneficial effects of colloidal iron on limiting further reduction^{3b} were evident in the transformation of **1b** to **2b** [74–82% in the presence of catalytic quantities of iron (experiments 10 and 11) and only 17% in its absence (experiment 9)]. In the case of phenanthrene itself, the corresponding percentages of 9,10-dihydrophenanthrene were 80% (experiment 5) and 57% (experiment 6), respectively. In 20 min, conversion of phenanthrene was essentially complete in the absence of iron (experiment 8) and 85% in its presence (experiment 7). Thus, phenanthrene tends to undergo over-reduction in the absence of iron and under-reduction in its presence; adjustment of the ratio of lithium to hydrocarbon appears to only partially compensate these tendencies. This "iron effect" appears to involve, as suggested earlier,^{3b} iron-catalyzed consumption of surplus lithium. In practice, it is convenient to employ excess lithium (3.5 g-atoms) and conduct reactions in the presence of iron (0.05 g-atom), taking advantage of the fact that the dihydrophenanthrenes are more

(1) This investigation was supported in part by Public Health Grant CA-8674 from the National Cancer Institute.

(2) Part VI: R. G. Harvey and C. C. Davis, *J. Org. Chem.*, **34**, 3607 (1969).

(3) (a) R. G. Harvey, L. Arzadon, J. Grant, and K. Urberg, *J. Amer. Chem. Soc.*, **91**, 4545 (1969); (b) R. G. Harvey and K. Urberg, *J. Org. Chem.*, **33**, 2206, 2570 (1968); (c) R. G. Harvey, *ibid.*, **32**, 238 (1967).

(4) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York, N. Y., 1961, p 425.

(5) 9,10-Dimethylanthracene was a notable exception in that *cis* and *trans* diastereomers were formed in equal proportion.

(6) W. Hückel and H. Bretschneider, *Ann.*, **540**, 157 (1939).

(7) S. Mejer, *Bull. Acad. Polon. Sci., Chim.*, **9**, 773 (1961).

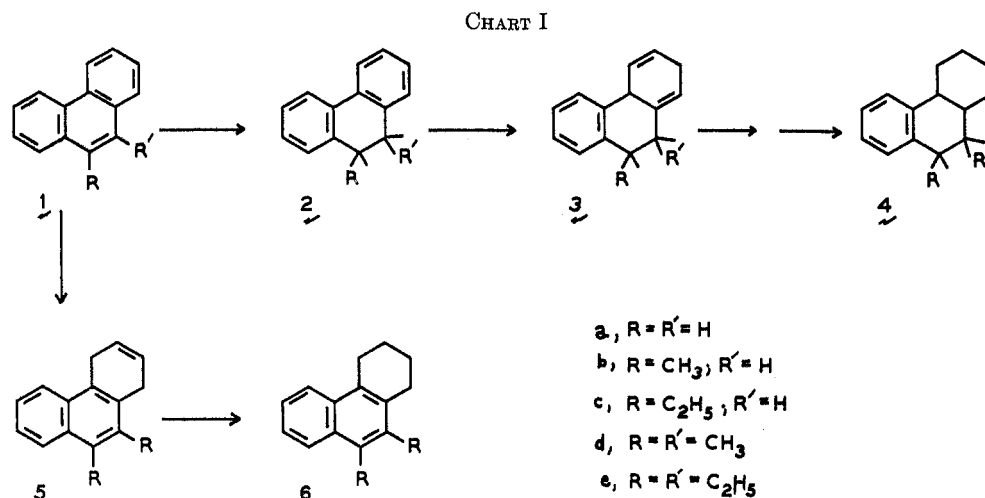


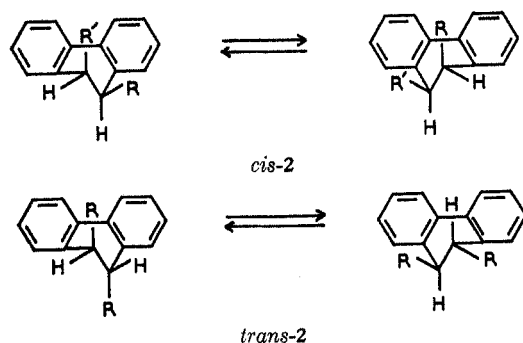
TABLE I
REDUCTION OF 1a-1e BY LITHIUM IN AMMONIA^a

Expt	Compd	Lithium, equiv	Method ^b	Time, min	Quench	Product composition, % ^c			
						1	2	3	Other
1	1a	2.5	A	120	Alcohol	43	51	0	6
2	1a	2.5	B	120	Alcohol	20	69	0	11
3	1a	2.5	A	120	H ₂ O	50	45	0	6
4	1a	2.5	B	120	H ₂ O	17	74	0	9
5	1a	3.5	A	60	H ₂ O	10	80	5	5
6	1a	3.5	B	60	H ₂ O	1	57	26	16
7	1a	3.5	A	20	H ₂ O	15	72	2	10
8	1a	3.5	B	20	H ₂ O	1	72	1	26
9	1b	2.5	B	60	Alcohol	0	17	49	34
10	1b	3.5	A	180	Alcohol	13	74	1	12
11	1b	5.0	A	180	Alcohol	2	82	7	9
12	1c	3.5	A	180	H ₂ O	7	86	0	7
13	1d	3.5	A	180	H ₂ O	2	72	9	17
14	1e	3.5	A	180	H ₂ O	21	61	2	17

^a Reaction conditions are described in the Experimental Section. ^b Ferric chloride (0.05 equiv) was added in method A and omitted in method B. ^c Percentages refer to integrated peak values from glpc (see Experimental Section).

readily separated from unreduced hydrocarbon than from the products of further reduction. Incidentally, water or alcohol proved almost equally effective as the quenching agent in these experiments.

9,10-Dimethyl- and 9,10-diethylphenanthrene underwent *stereospecific reduction* to provide the corresponding *cis*-9,10-dialkyl-9,10-dihydrophenanthrenes (*cis*-2d and -2e). The *cis* assignment was deduced from variable-



temperature nmr studies⁸ in comparison with the corresponding *trans* diastereomers (*trans*-2d and -2e), which were independently synthesized *via* alkylation of the corresponding 9-alkyl-10-lithio-9,10-dihydrophenan-

threne obtained from treatment of 9-methyl- or 9-ethyl-9,10-dihydrophenanthrene with *n*-butyllithium in TMEDA.⁹ The nmr data on *cis*-2d, reported in prior communication,⁸ revealed rapid (nmr time scale) conformational inversion (*i.e.*, the appearance of only one average signal for both the axial and the equatorial groups) at ambient temperature. Lowering of the temperature produced coalescence of the methyl doublet, and ultimately (-80°) the formation of two doublets of the same intensity equally spaced on either side of the original doublet center. The coalescence temperature was -47° , and $\Delta F^\ddagger = 10.8$ kcal/mol. Similarly, the nmr spectrum of *cis*-2e at low temperature (-20°) showed the presence of a "frozen" conformation having an axial and an equatorial substituent; the methyl protons appeared as a single triplet at higher temperature (80°). The coalescence temperature was 27° , and $\Delta F^\ddagger = 14.9$ kcal/mol for the ring inversion process. In contrast, the corresponding *trans* isomers showed temperature-independent nmr spectra from -80 to 150° . Since molecular models indicate significant group interactions in the *trans* diequatorial but not in the *trans* diaxial conformers, a preferred diaxial conformation appears probable.

A *cis* specificity of reduction of 9,10-dialkylphenanthrenes is consistent with the previously observed *trans*

(8) P. W. Rabideau, R. G. Harvey, and J. B. Stothers, *Chem. Commun.*, 1005 (1969).

(9) TMEDA = N,N,N',N'-tetramethylethylenediamine.

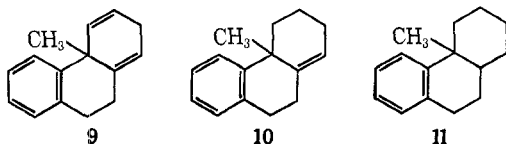
specificity of analogous transformation of 9,10-dialkylanthracenes. In both series, the favored isomer contains one substituent in the axial orientation while the other is equatorial. Similar factors apparently govern these conformational preferences (see Discussion).

Minor products may arise either *via* alternative modes of reduction (*e.g.*, **5**) or through further transformation of the 9,10-dihydrophenanthrenes.¹⁰ Glpc analysis of the products derived from reduction of phenanthrene revealed only very minor quantities (1–2%) of other dihydrophenanthrene isomers. Somewhat larger percentages (5–10%) were obtained from the 9-mono- and 9,10-dialkylphenanthrenes. A compound whose nmr and mass spectral properties were consistent with the structure of 1,4-dihydro-9,10-dimethylphenanthrene (**5d**) was isolated from glpc separation of products from 9,10-dimethylphenanthrene. A related tetrahydro derivative was similarly detected in the products from 9,10-diethylphenanthrene and identified as 9,10-diethyl-1,2,3,4-tetrahydrophenanthrene (**6d**).

The second-stage reduction product of phenanthrene reverted to 9,10-dihydrophenanthrene on standing. Its uv spectrum [$\lambda_{\max}^{\text{EtOH}}$ 234 m μ (ϵ 1200)] indicated absence of the styrenoid chromophore, eliminating from consideration the two conjugated isomeric structures **7** and **8**. The alternative unconjugated structure,



2,4a,9,10-tetrahydrophenanthrene (**3a**), was consistent with both the uv and nmr spectra. The latter exhibited aromatic protons at δ 7.1 (m, 4), vinyl protons as multiplets at 6.4 (1) and at 5.8 (2), and complex multiplets at 2.7 and 2.2 (7 total). The structure of **3a** was further confirmed by reductive methylation of 9,10-dihydrophenanthrene in liquid ammonia² to provide the methyl homolog, 4a-methyl-2,4a,9,10-tetrahydrophenanthrene (**9**). The nmr spectrum of the latter showed analogous protons at δ 7.3 (m, 4, aromatic), 6.3 (d, 1, CH=C, $J = 10$ Hz), 5.9 and 5.7 (m, 2, CH=CH), and 2.7 (m, 6, CH₂) in addition to a methyl singlet at 1.5. Catalytic hydrogenation of **9** furnished the monoolefin **10** (60%) and the saturated derivative **11** (40%). The nmr spectrum of the latter agreed with that for **11** synthesized by a different route.¹¹



The alkylphenanthrene derivatives required in these studies were synthesized *via* the related lithiophenanthrene derivatives by a modification of the method of Mikhailov and Chernova.¹² Thus, reaction of 9-lithiophenanthrene (obtained from exchange between

9-bromophenanthrene and *n*-butyllithium) with methyl and ethyl iodides provided 9-methyl- and 9-ethylphenanthrene, respectively. Repetition of this sequence on the 9-monoalkylphenanthrenes furnished the 9,10-dialkylphenanthrenes. Introduction of the second substituent proved appreciably more difficult, necessitating employment of more vigorous conditions. More satisfactory yields were obtained with the alkyl iodides than with the bromides, and it was found advantageous to employ ethyllithium in preference to *n*-butyllithium in the ethylations (to avoid mixed products).

Discussion

The remarkable stereospecificity of reduction of 9,10-dialkylphenanthrene parallels that recently demonstrated in the anthracene and benz[*a*]anthracene series.^{3a} An analogous mechanism would require initial axial protonation at one position of the 9,10 dianion (**12**), followed by conformational equilibration and axial protonation at the second position (Chart I).

Attempts to demonstrate the existence of a dianion have, however, been unsuccessful. Thus, the product of interaction of lithium (2.5 g-atoms) with phenanthrene in liquid ammonia failed to undergo alkylation with methyl bromide, ethyl bromide, or benzyl chloride, providing instead 9,10-dihydrophenanthrene as the major product. In contrast, the anthracene 9,10 dianion under comparable conditions underwent quantitative dialkylation with *cis* stereospecificity.¹³ It appears probable that within the time limits of these experiments (10–20 min) no appreciable concentration of mono- or dinegative ions of phenanthrene¹⁴ are present in ammonia at -33° . Facile protonation of anionic intermediates by ammonia (eq 1) is consistent

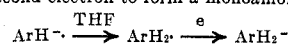


with Wooster's rule¹⁵ that carbanion stability in liquid ammonia requires at least two substituent aromatic rings.¹⁶

The observed stereospecificity is explicable in terms of a modified mechanism resembling the dianion mechanism in that final protonation is product determining, but involves alternate addition of electrons and protons (Chart II). Protonation of **13** may be expected to occur

(13) R. G. Harvey and L. Arzadon, *Tetrahedron*, in press.

(14) The electronic spectrum of the mononegative ion formed between phenanthrene and sodium in tetrahydrofuran or dimethoxyethane has been reported.^{15,16} However, little is known concerning the dinegative ion whose spectrum in the same solvents could not be obtained¹⁶ "owing to its decomposition and the low electron affinity of the monovalent ion." Electrical conductivity measurements¹⁷ reported to indicate slow formation of a diamagnetic species under similar conditions may reflect this decomposition, which may be a consequence of proton abstraction from the solvent followed by acquisition of a second electron to form a monoanion.



(15) D. E. Paul, D. Lipkin, and S. I. Weissman, *J. Amer. Chem. Soc.*, **78**, 116 (1956).

(16) P. Balk, G. J. Hoijsink, and J. W. H. Schreurs, *Rec. Trav. Chim. Pays-Bas*, **76**, 813 (1957).

(17) T. L. Chu and S. C. Yu, *J. Amer. Chem. Soc.*, **76**, 3367 (1954).

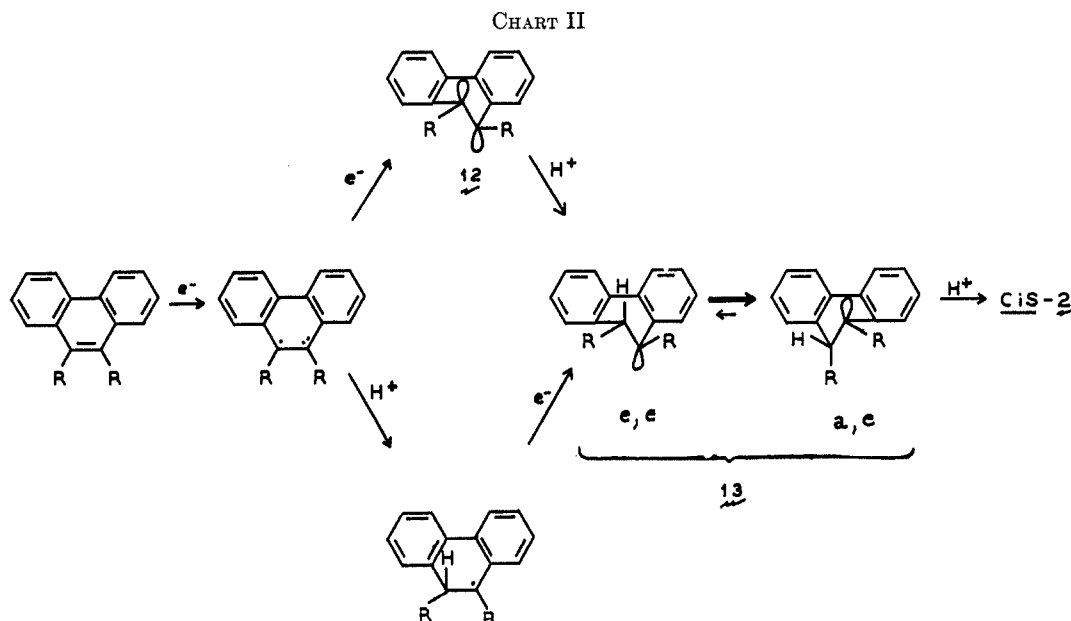
(18) C. B. Wooster and N. W. Mitchell, *ibid.*, **52**, 688 (1930); C. B. Wooster and J. F. Ryan, *ibid.*, **54**, 2419 (1932); **56**, 1133 (1934).

(19) Detection of anionic intermediates of anthracene or phenanthrene by decomposition with deuterium oxide proved inconclusive. In ammonia, rapid exchange with the solvent ($\text{NH}_3 + \text{D}_2\text{O} \rightleftharpoons \text{N}^+\text{H}_2\text{D} + ^-\text{OD}$) is apparently responsible for the low, statistical level of incorporation. Evaporation of the ammonia before deuteration proved equally unsatisfactory, possibly owing to the instability of these dinegative ions in organic solvents.¹⁴

(10) Base-catalyzed isomerization of double bonds and disproportionation of radical-anionic intermediates are alternative possibilities; analogous processes were not detected in previous investigations of other hydrocarbons.⁹

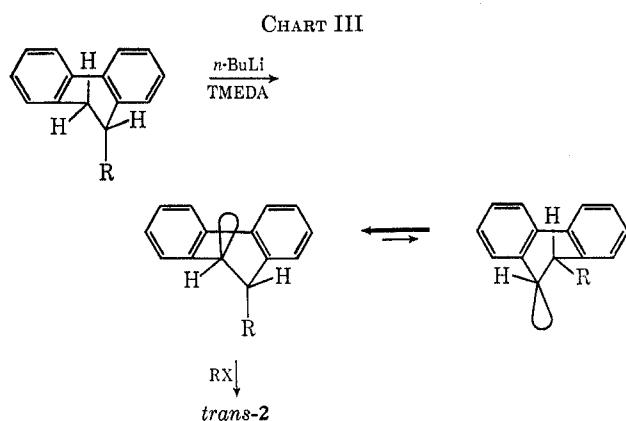
(11) V. Boekelheide and E. Sturm, *J. Amer. Chem. Soc.*, **91**, 902 (1969).

(12) B. M. Mikhailov and N. E. Chernova, *Zh. Obshch. Khim.*, **21**, 1517 (1951).



from the axial direction to allow maximum orbital overlap of the electron pair with the adjacent aromatic ring. Also, steric interaction between the alkyl groups of the diequatorial conformer of **13** may be expected to favor the inverted form (**13a** and **13e**) in which the groups are one axial, one equatorial. Protonation of **13a** and **13e** leads to the experimentally observed *cis* isomer.

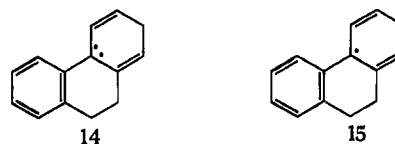
Consistent with this scheme is the preparation of the corresponding *trans* isomers through alkylation of the 9-methyl and 9-ethyl-9,10-dihydrophenanthrenes (Chart III). In these cases, the lone substituents in the monoanions are free to assume relatively unhindered axial positions while the adjacent electron pairs occupy orbitals oriented axially in the other direction. Alkylation of these intermediates may be expected to lead to the observed *trans* products.



Attempted base-catalyzed equilibration of *cis*- or *trans*-**2e** under conditions comparable with those used for their synthesis failed to result in any detectable isomerization. This result is consistent with the proposed mechanism and with previous observations in the anthracene series.^{3a} Presumably, proton abstraction and proton return occur from the same direction (axial), resulting in zero net change. In any event, failure to isomerize affirms the concept of kinetically controlled reduction and alkylation.

The hybridization of the anionic intermediates represented as sp^3 in Charts II and III undoubtedly lies between the extremes of sp^3 and sp^2 geometry; the observed stereochemical results may be similarly and equally well explained on the basis of either assumption. The calculated⁴ π -electron densities of the *o*-phenylbenzyl anion indicate that approximately 52% of the charge resides on the α -carbon atom, suggesting a configuration between pyramidal and planar. Other factors, such as the extent of association of the Li cation and solvation of the latter by NH_3 and THF, though difficult to estimate, probably also play a role in the determination of product geometry.

During the second stage of reduction, partial protonation by ammonia takes place, as evidenced by failure to alkylate at the 2 position. Methylation, however, occurred with facility at **4a** to provide the angular methyl derivative, **9**. While direct evidence concerning the intermediate involved is lacking, an anionic structure, such as **14**, appears more probable on grounds of the expected susceptibility to reduction of the related radical structure **15**, which is both benzylic and penta-dienyl.



Direct synthesis of **9** *via* reductive methylation of phenanthrene itself took place when sufficient lithium (5 g-atoms) was employed. This novel method of angular methylation holds considerable synthetic promise, and application to various systems is currently under investigation.

Experimental Section

Physical Data.—Proton nmr spectra were obtained on a Varian A-60 or A-60A spectrometer; chemical shifts are reported relative to tetramethylsilane in $CDCl_3$ or CCl_4 . Gas chromatographic analyses were performed on a F & M Model 500 chromatograph employing either a 6 ft \times 0.25 in. 5% DEGS on 60-80 mesh Chromosorb W column (A) or a similar column containing 10%

of the liquid phase (B). Quantitative glpc data were verified by internal standard and product recovery and found to be generally reliable. Infrared and ultraviolet spectra were obtained on Perkin-Elmer Infracord, Model 137, and Cary II spectrometers, respectively. Microanalyses were performed by Micro-Tech Laboratories, Skokie, Ill. and Galbraith Laboratories, Knoxville, Tenn.

9-Bromophenanthrene.—Bromine (0.275 mol, 14 ml) in acetic acid (25 ml) was added dropwise over 30 min to a warm (40°) solution of phenanthrene (0.25 mol, 44.5 g) in acetic acid (350 ml). The resulting suspension was stirred at 40° for 1.5 hr, cooled to 20°, filtered, and washed with petroleum ether. The pale yellow product was slurried in cold ether (150 ml), filtered, and washed twice with 50-ml portions of cold ether to give phenanthrene dibromide (61.0 g, 72%). This was heated on a steam bath for 2 hr until evolution of HBr ceased, then recrystallized from absolute ethanol (300 ml) (charcoal) to provide 33 g of 6-bromophenanthrene, mp 62–63° (lit.²⁰ mp 65–66°; concentration of the mother liquor afforded an additional 8 g (65% overall).

9-Methylphenanthrene (1b).—*n*-Butyllithium (0.12 mol, 1.6 M in hexane) was added dropwise to 9-bromophenanthrene (0.09 mol, 23 g) in anhydrous ether (100 ml). Stirring was continued for 30 min after addition, and methyl iodide (0.2 mol, 28 g) was added dropwise. The mixture was refluxed for 1.5 hr and quenched by the addition of water. The organic layer was washed several times with water, dried, and evaporated. Recrystallization from hexane gave 1b: yield 14.2 g (82%); mp 90–91° (lit.¹² mp 90.5–91.5°).

9-Ethylphenanthrene (1c).—Analogous reaction of ethyllithium (1.2 M in hexane) with 9-bromophenanthrene (0.12 mol, 31 g) furnished crude 1c as an oil. The latter, upon heating with petroleum ether (100 ml) followed by refrigeration, crystallized as tiny white needles: yield 21 g (85%); mp 61.5–62.5° (lit.¹² mp 60–61.5°).

9-Bromo-10-methylphenanthrene.—Bromine (0.055 mol, 2.8 ml) was added dropwise to a solution of 9-methylphenanthrene (0.05 mol, 9.7 g) in acetic acid (200 ml). After 12 hr, the precipitate was filtered, washed until neutral, and dried to afford 7.85 g of 9-bromo-10-methylphenanthrene, mp 118–120°. The addition of water to the original filtrate produced a second crop (1.8 g) after recrystallization from ethanol: mp 119.5° (lit.¹² mp 120.5–122.5°); total yield 71%.

9,10-Dimethylphenanthrene (1d).—*n*-Butyllithium (0.075 mol, 1.6 M in hexane) was added dropwise to 9-bromo-10-methylphenanthrene (0.03 mol, 8.0 g) in anhydrous ether. The solution was stirred for 5 min before addition of methyl iodide (0.075 mol, 4.7 ml). The vigorous reaction which ensued was quenched 10 min later and worked up as usual to afford 4.1 g (65%) of 1d as white needles, mp 143–146° (lit.²¹ mp 143–144.5°).

9-Bromo-10-ethylphenanthrene.—Bromine (0.1 mol, 16 g) in acetic acid (20 ml) was added dropwise to a warm solution of 9-ethylphenanthrene (0.09 mol, 19 g) in acetic acid (150 ml). After 20 hr, the mixture was poured into dilute bisulfite solution and filtered to provide a white solid, purified by passage through a column of basic alumina (eluted with petroleum ether). A portion (10 g) of the oily product crystallized from ether–hexane on cooling to afford 9-bromo-10-ethylphenanthrene as white needles, mp 69.5–70°. The remainder of the product (10 g) crystallized upon standing, and was triturated with hexane to provide a combined yield of 16.3 g (62%) of 9-bromo-10-ethylphenanthrene.

Anal. Calcd for C₁₆H₁₃Br: C, 67.38; H, 4.59; Br, 28.02. Found: C, 67.16; H, 4.59; Br, 27.83.

9,10-Diethylphenanthrene (1e).—Ethyllithium (0.07 mol, 1.2 M in hexane) was added dropwise to a solution of 9-bromo-10-ethylphenanthrene (0.04 mol, 11.6 g) in anhydrous ether (75 ml). After 2 hr, ethyl iodide (0.15 mol, 23.2 g) was added from a dropping funnel and the mixture was maintained at reflux for 1.5 hr. The oily product crystallized from cold petroleum ether to afford 3.0 g of 1e, mp 104–105° (lit.²¹ mp 105–106°).

Lithium–Ammonia Reduction.—Precautions for the exclusion of impurities (moisture, air, peroxides, ferrous metals) were scrupulously observed; all reductions were carried out under helium rather than nitrogen for reasons stated earlier.³ Tetra-

hydrofuran (THF) was freshly distilled from CaH₂ before use. Ammonia was distilled into the reaction vessel through a column of barium oxide (10–20 mesh). Lithium wire (Lithium Corp. of America) was wiped free of oil and washed with hexane immediately before use.

All reductions in ammonia were carried out in a Morton flask employing the conditions described for reduction of 9-methylphenanthrene, unless specified otherwise.

9-Methyl-9,10-dihydrophenanthrene (2b).—A solution of 1b (2.5 mmol, 0.48 g) in THF (38 ml) was added to refluxing ammonia (75 ml) containing FeCl₃ (20 mg). To this was added lithium wire (3.5 equiv, 0.043 g). Reaction was quenched after 3 hr by addition of ethanol and then water. Glpc on column A at 150° showed 74% 2b (*t*_R 3.6 min), 13% 1b (*t*_R 12.5 min,) and a variety of miscellaneous products. Repetition on a larger scale and distillation of the product provided 2b: bp 121° (1.5 mm) [lit.²² bp 158–160° (9 mm)]; nmr (CDCl₃) δ 7.8 (m, 2, aromatic), 7.3 (m, 6, aromatic), 2.9 (m, 3, benzylic), and 1.2 (d, 3, *J* = 6 Hz, CH₃).

***cis*-9,10-Dimethyl-9,10-dihydrophenanthrene (*cis*-2d).**—Analogous reaction of 1d furnished an oil containing 72% 2d according to glpc analysis on column A at 150°. The analytical sample of 2d, trapped off the glpc column, exhibited nmr (CDCl₃) δ 7.7 (m, 2, aromatic), 7.3 (m, 6, aromatic), 3.0 (m, 2, benzylic), and 1.1 (d, 6, *J* = 6.5 Hz, CH₃). The *cis* assignment is based on variable-temperature nmr studies reported separately.⁸

Anal. Calcd for C₁₆H₁₈: C, 92.26; H, 7.74. Found: C, 92.22; H, 7.82.

A second oily product, also obtained from the glpc column, was identified as 1,4-dihydro-9,10-dimethylphenanthrene (5d, 9%) from its spectral properties: nmr (CDCl₃) δ 7.9 and 7.4 (m, 4, aromatic), 6.0 (s, 2, vinyl), 3.55 (m, 4, allylic), 2.6 (s, 3, CH₃), and 2.3 (s, 3, CH₃); mass spectrum *m/e* 208 (calcd mol wt, 208).

9-Ethyl-9,10-dihydrophenanthrene (2c).—Reduction of 1c (10 mmol, 2.0 g) under the conditions employed with the methyl homolog provided crude 2c (86% by glpc on column A). Chromatography on silica gel (hexane) separated 2c from 1c (7%) and a similar amount of products of further reduction. Compound 2c was an oil: nmr (CCl₄) δ 7.6 (m, 2, aromatic), 7.2 (m, 6, aromatic), 2.9 (m, 3, benzylic), 1.3 (q, 2, *J* = 6.5 Hz, CH₂CH₃), and 0.9 (t, 3, *J* = 6.5 Hz, CH₃).

Anal. Calcd for C₁₆H₁₈: C, 92.26; H, 7.74. Found: C, 92.19; H, 7.74.

***cis*-9,10-Diethyl-9,10-dihydrophenanthrene (*cis*-2e).**—Reduction of 1e under standard conditions provided an oil containing 61% *cis*-2e (*t*_R 5.0 min on column A at 150°). An analytical sample of *cis*-2e obtained from the gas chromatograph was an oil for which variable-temperature nmr studies are separately reported.⁸

Anal. Calcd for C₁₈H₂₀: C, 91.47; H, 8.53. Found: C, 91.70; H, 8.36.

A second oily product (11%) isolated in similar manner (*t*_R 11 min) was identified as 9,10-diethyl-1,2,3,4-tetrahydrophenanthrene (6d): nmr (CDCl₃) δ 8.0 and 7.4 (m, 4, aromatic), two methylene doublets centered at 2.82 and 3.11 (*J* = 7.5 Hz) superimposed on a low, wide multiplet (total integral of 8), 1.9 (m, 4, CH₂), 1.3 (t, 3, *J* = 7.5 Hz, CH₃), and 1.2 (t, 3, *J* = 7.5 Hz, CH₃); mass spectrum *m/e* 238 (parent peak).

***trans*-9,10-Dimethyl-9,10-dihydrophenanthrene (*trans*-2d).**—*n*-Butyllithium (10 mmol, 1.6 M in hexane) was added to a cold solution of 2b (0.98 g, 5 mmol) in hexane (5 ml) and N,N,N',N'-tetramethylethylenediamine (10 ml). The solution was allowed to stand for 4 days at 0°, and a stream of methyl bromide was passed into it for 15 min. The reaction mixture was then quenched with water; ether was added; and the organic layer was washed with water, dilute HCl, and water, and then dried and evaporated. Glpc analysis on column B at 140° showed ca. 20% *trans*-2d²³ (*t*_R 4.4 min), 30% 1b (*t*_R 7.4 min), and 15% unknown product (*t*_R 9.3 min). An analytical sample of *trans*-2d trapped from the gas chromatograph was an oil for which variable-temperature nmr studies are separately reported.^{8,23}

Anal. Calcd for C₁₆H₁₈: C, 92.26; H, 7.74. Found: C, 92.17; H, 7.85.

***trans*-9,10-Diethyl-9,10-dihydrophenanthrene (*trans*-2e).**—*n*-Butyllithium (12 mmol, 1.6 M in hexane) was added dropwise to

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(21) C. K. Bradsher and W. J. Jackson, Jr., *J. Amer. Chem. Soc.*, **76**, 4140 (1954).

(22) H. Rapoport and A. R. Williams, *ibid.*, **71**, 1774 (1949).
(23) The *trans* assignment is based on the fact that the "frozen-out" conformations exhibited only one type of substituent whereas the *cis* diastereomers exhibited axial and equatorial groups in equal proportion.⁸

a solution of **2c** (1.4 g, 6.7 mmol) in cyclohexane (20 ml) and TMEDA (1.6 ml) at 10°. The solution was allowed to stand at 0° for 65 hr before addition of ethyl iodide (30 mmol, 2.3 ml), then stirred for 2 hr at ambient temperature. The reaction mixture was quenched by water and worked up in conventional manner to provide an oil. Glpc analysis on column B at 160° showed 25% *trans-2e*²³ (*t_R* 5.3 min) together with 65% unreacted starting material (*t_R* 8.0 min). A pure sample of *trans-2e* was obtained from glpc. Variable-temperature nmr studies confirming the structure and providing evidence regarding its conformation are reported elsewhere.^{8,23}

Anal. Calcd for C₁₅H₂₀: C, 91.47; H, 8.53. Found: C, 91.28; H, 8.87.

2,4a,9,10-Tetrahydrophenanthrene (3a).—Lithium-ammonia reduction of 9,10-dihydrophenanthrene (5 mmol, 0.9 g) was quenched with water after 2 hr and the product was isolated by extraction (as rapidly as possible) with ether. Glpc analysis on column B at 175° indicated 62% **3a** (*t_R* 3 min), 23% **2a** (*t_R* 4 min), 2% *as*-octahydrophenanthrene (*t_R* 1.6 min), and minor products. Although **3a** underwent spontaneous reversion to **2a** on standing, it was sufficiently stable to obtain nmr and uv spectra of a sample trapped off the gas chromatograph: nmr δ 7.1 (m, 4, aromatic), 6.4 (d, 1, *J* = 10 Hz, vinyl), 5.8 (m, 2, vinyl), and 2.7 and 2.2 (complex multiplets, 7 protons); uv max (95% ethanol) 234 m μ (ϵ 1200).

Analogous reaction conducted in the absence of ferric chloride provided **3a** (32%), further reduction products (49%), and recovered **2a** (19%).

4a-Methyl-2,4a,9,10-tetrahydrophenanthrene (9).—To a solution of phenanthrene (20 mmol, 2.6 g) in THF (100 ml) and ammonia (250 ml) was added lithium (5 equiv, 0.69 g). The dark green-blue color was discharged 5 min later by methyl bromide. Conventional work-up provided an oil, glpc analysis of which on

column B at 125° showed 93% **9** (*t_R* 7.2 min). Distillation through a short Vigreux column gave 1.5 g of **9** as a colorless oil: bp 109°; nmr data cited in Results.

Anal. Calcd for C₁₅H₁₆: C, 91.78; H, 8.22. Found: C, 91.52; H, 8.36.

Catalytic hydrogenation of **9** (838 mg, 4.27 mmol) in 95% ethanol (10 ml) over a platinum catalyst (10 mg of PtO₂) in a "Vortex Low Pressure Hydrogenation Apparatus" (J. B. Thompson Co.) at 28 lb and 30° for 18 hr resulted in absorption of 1.4 equiv of hydrogen. Two products were isolated from glpc (column B at 100°). The first (*t_R* 10 min) proved to be **10** (60%): nmr (CCl₄) δ 7.0 (4 aromatic protons), 5.4 (1 vinyl), 2.8 (m, 2, benzylic), 2.6–1.5 (m, 8), and 1.4 (s, 3, CH₃).

Anal. Calcd for C₁₅H₁₈: C, 90.85; H, 9.15. Found: C, 90.38; H, 9.38.

The second product of hydrogenation (*t_R* 7 min) was **11** (40%), whose nmr spectrum corresponded with that recently reported by Boekelheide and Sturm.¹¹

Anal. Calcd for C₁₅H₂₀: C, 89.93; H, 10.06. Found: C, 89.80; H, 10.05.

Registry No.—**1a**, 85-01-8; **1b**, 883-20-5; **1c**, 3674-75-7; **1d**, 604-83-1; **1e**, 15810-14-7; **2c**, 22139-41-9; *cis-2d*, 22140-64-3; *trans-2d*, 22140-65-4; *cis-2e*, 22155-45-9; *trans-2e*, 22140-66-5; **5d**, 22139-42-0; **6d**, 22139-43-1; **9**, 22139-44-2; **10**, 22139-45-3; 9-bromo-10-ethylphenanthrene, 17918-49-9.

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A Preparation of 9,10-Dicyanoanthracene and 9,10-Dicyanophenanthrene by Cyanation of the Respective 9-Cyanoarenes¹

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Carbanion intermediates formed by reaction of sodium cyanide with 9-cyanoanthracene and 9-cyanophenanthrene are oxidized in high yield by sodium 9,10-anthraquinone- α -sulfonate in dimethyl sulfoxide to give the 9,10-dinitriles, and in the former case the yield is almost theoretical; the cyanoarenes are themselves prepared in excellent yield from the corresponding bromo compounds with cuprous cyanide in dimethyl sulfoxide. Whereas the 9-cyanoanthracene-cyanide mixture shows signs of electron exchange and is oxygenated, the 9-cyanophenanthrene-cyanide mixture exhibits neither of these properties.

Sodium 9,10-anthraquinone- α -sulfonate (α -SAS) recently has been shown to be a most expedient reagent for the abstraction of hydride ions from certain preformed carbanions;² such carbanions have been generated in dipolar aprotic solvents, especially dimethyl sulfoxide (DMSO), by the facile reaction of cyanide ion with hydrocarbons possessing a polarized carbon-carbon double bond. The attack of cyanide ion upon a derivative of an aromatic system, 9-nitroanthracene, was the subject of a previous publication from this laboratory,³ and, because of the remarkable reactivity exhibited by this compound, we have now examined the reaction of sodium cyanide with the 9-cyano derivatives of anthracene and phenanthrene. The incidental formation of the 9,10-dinitriles of anthracene³ and phenanthrene⁴ in experiments where the corresponding cyano nitro compounds were prepared in aprotic

solvents with alkali metal cyanides provided a precedent for the choice of the particular cyanoarenes as substrates.

Treatment of DMSO solutions⁵ of the 9-cyanoarenes, under nitrogen, with sodium cyanide in the presence of α -SAS, resulted in the immediate formation of an intense magenta color. This color has been evident in previous cyanation reactions employing this oxidizing agent,² and its generation is considered due to the formation of the hydroquinone ion. Its appearance therefore provides a visual indication that an oxidation-reduction process is taking place and that, in turn, there has been a reaction between the substrate and sodium cyanide. This color indication is particularly helpful if a solution of the substrate and sodium cyanide does not develop any color of its own, as was found to be the case with 9-cyanophenanthrene.

The cyanation of 9-cyanoanthracene with sodium cyanide and α -SAS was accomplished very smoothly, and a 94% yield of the 9,10-dinitrile was achieved from

(1) Grateful acknowledgement is made to the U. S. Army Research Office [grants DA-ARO(D)-G679 and G857] for the support of this work.

(2) K. E. Whitaker, B. E. Galbraith, and H. R. Snyder, *J. Org. Chem.*, **34**, 1411 (1969).

(3) R. G. Landolt and H. R. Snyder, *ibid.*, **33**, 403 (1968).

(4) W. L. Mosby, *ibid.*, **24**, 421 (1959).

(5) DMSO was chosen for the solvent as it is superior to DMF for dissolving α -SAS.