477. *The Synthesis of 4 : 5-Dimethylphenanthrene.*

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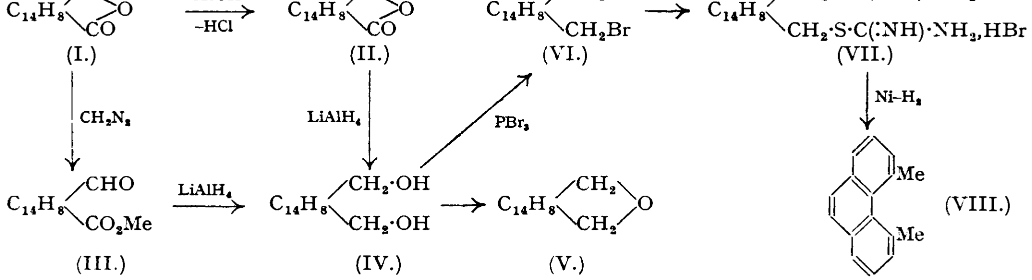
A series of convenient reactions for the preparation, from pyrene, of 4 : 5-dimethylphenanthrene and some of its derivatives is described. Ultra-violet absorption data for the hydrocarbon indicate the absence of any marked steric inhibition of resonance.

Phenanthrene derivatives with methyl substituents in the 4- and the 5-position are of considerable interest from the point of view of the nature of the steric hindrance associated with such a structure (Cook, *Ann. Reports*, 1942, **39**, 172; cf. Cook and Kennaway, *Amer. J. Cancer*, 1938, **33**, 55; Newman *et al.*, *J. Amer. Chem. Soc.*, 1940, **62**, 2295; 1947, **69**, 3023; 1948, **70**, 1913; Campbell, Ph.D. Thesis, Glasgow, 1949). Unsuccessful attempts to synthesise the parent hydrocarbon, 4 : 5-dimethylphenanthrene, have been reported by Haworth and Sheldrick (*J.*, 1934, 1950; cf. *ibid.*, p. 456) and by Lewis and Elderfield (*J. Org. Chem.*, 1940, **5**, 290). The ready preparation of 4-formyl phenanthrene-5-carboxylic acid (I) by the ozonisation of pyrene (Vollmann *et al.*, *Annalen*, 1937, **531**, 1; Fieser and Novello, *J. Amer. Chem. Soc.*, 1940, **62**, 1855) suggested the following route for its synthesis; this has been accomplished and the yield at every stage was of the order of 80%.



($C_{14}H_8$ represents the phenanthrene nucleus substituted at positions 4 and 5.)

The aldehydo-acid was found not to give derivatives with carbonyl reagents; its constitution is therefore best represented by the lactol structure (I). Esterification of the acid with methanolic hydrogen chloride gave the corresponding ψ-ester (II), which likewise gave no carbonyl derivatives. Treatment of the acid with diazomethane, however, furnished an isomeric methyl ester, which, as it readily gave a 2 : 4-dinitrophenylhydrazone, almost certainly possessed the structure (III). Reduction of either of these methyl esters with lithium aluminium hydride (cf. *inter al.*, Nystrom and Brown, *J. Amer. Chem. Soc.*, 1947, **69**, 1197) furnished 4 : 5-bishydroxymethylphenanthrene (IV) in excellent yield. The action of hydrogen chloride on this diol did not furnish the expected bischloromethyl compound, the only product formed being the cyclic ether (V). The corresponding bisbromomethyl compound (VI), however, was found to be readily obtainable by the action of phosphorus tribromide on the diol. Attempts to reduce (VI) directly to 4 : 5-dimethylphenanthrene were surprisingly unsuccessful; catalytic hydrogenation and lithium aluminium hydride reduction both gave the cyclic ether (V) as the sole isolable product. The bisbromomethyl compound was therefore treated with thiourea to give a quantitative yield of the di*iso*thiuronium dibromide (VII) which underwent smooth hydrogenolysis with Raney nickel to furnish the required 4 : 5-dimethylphenanthrene.

This work was nearing completion at the time of publication of the paper by Newman and Whitehouse (*J. Amer. Chem. Soc.*, 1949, **71**, 3664) who prepared 4 : 5-dimethylphenanthrene in 17% yield by fission of the cyclic ether (V) with phosphorus and hydriodic acid at 165° for 17 hours. The smooth low-temperature reactions used in the present work are preferable to this drastic procedure with the risk of molecular rearrangement. The physical constants of our hydrocarbon and its derivatives agreed well with the corresponding data of the American workers.

The ultra-violet absorption data (in ethanol) for the 4 : 5-substituted phenanthrenes were kindly determined by Dr. E. A. Braude and the results are tabulated below.

Compound.	$\lambda_{max.}$, A.	ε.	Compound.	$\lambda_{max.}$, A.	ε.	Compound.	$\lambda_{max.}$, A.	ε.
(I)	2510	34,000	(IV)	2580	55,000	(III)	2720	25,000
	2580	34,000		2920	9,000		2800	24,000
	2650	34,000		3010	11,000		*3560*	1,500
	2760	30,000		3120	11,000			
	3480	1,500				(VI)	*2600*	30,000
	3650	1,500	(V)	2580	52,000		2700	34,000
				2810	12,000		2800	30,500
(II)	2510	30,500		2910	10,000		*3010*	13,000
	2580	33,000		3010	10,000		*3130*	10,000
	2670	30,500						
	3460	1,000	(VIII)	2580	38,000	(VII)	2700	36,000
	3640	1,000		2910	8,000		*2770*	32,000
				3020	11,500		*3040*	10,000
				3140	11,500			

(Italicised wave-lengths refer to inflections.)

It can be seen that the spectra fall into two well-defined groups. The first, comprising the aldehydo-acid (I), the ψ-ester (II), the bishydroxymethyl compound (IV), the cyclic ether (V), and 4 : 5-dimethylphenanthrene itself (VIII), consists of absorption curves which are definitely "phenanthrenoid" in character, although some of the fine structure exhibited by phenanthrene itself has been smoothed out. This may be taken to indicate that in these compounds the steric hindrance associated with 4 : 5-substitution does not affect the uniplanarity of the phenanthrene nucleus. The second group, containing the methyl ester (III), the di*iso*thiuronium dibromide (VII), and the bisbromomethyl compound (VI), is characterised by a single region of maximal absorption with practically no fine structure. It would seem that in these three compounds with very bulky substituents at positions 4 and 5, there is considerable distortion of the phenanthrene nucleus with consequent inhibition of resonance.

EXPERIMENTAL.

4-*Formylphenanthrene*-5-*carboxylic Acid* (I).—A modification of the method of Vollmann *et al.* (*loc. cit.*) was adopted. Pyrene (10 g.) was dissolved in carbon tetrachloride (250 c.c.) and a stream of ozonised oxygen (5% O_3) was passed through the solution for 16 hours. As pyrene ozonide is insoluble in carbon tetrachloride, it is precipitated from the solution and is thus protected from further ozonisation. The carbon tetrachloride was then removed in steam, and the residue worked up as described by the German authors. From the reaction were obtained unchanged pyrene (5·8 g.) and the aldehydo-acid (3·7 g.; conversion 42%; yield 71%). The acid was recovered unchanged after treatment with alcoholic 2 : 4-dinitrophenylhydrazine sulphate and semicarbazide acetate.

ψ-Methyl Ester (II).—A suspension of the aldehydo-acid (1 g.) in methanol (40 c.c.) was saturated with hydrogen chloride and heated under reflux for 2 hours. The solvent was removed, and the residue treated with sodium carbonate solution. The insoluble material was crystallised from methanol, giving the *ψ-ester* (II) as needles, m. p. 176—177° (Found : C, 77·0; H, 4·6. $C_{17}H_{12}O_3$ requires C, 77·2; H, 4·6%). Like the parent acid, this ester exhibited no carbonyl reactivity.

Methyl Ester (III).—The finely-powdered aldehydo-acid (3·6 g.) was suspended in acetone (50 c.c.) and treated with an excess of ethereal diazomethane; the solution was kept at room temperature for 16 hours, all the solid then having dissolved. Removal of the solvent and crystallisation from methanol gave the *methyl* ester (2·9 g.) as needles, m. p. 113—114° (Found : C, 77·1; H, 4·8. $C_{17}H_{12}O_3$ requires C, 77·2; H, 4·6%). The action of methanolic 2 : 4-dinitrophenylhydrazine sulphate yielded the corresponding 2 : 4-*dinitrophenylhydrazone* as orange prisms, m. p. 250°, from methanol (Found: N, 12·65. $C_{13}H_{16}O_6N_4$ requires N, 12·6%).

No recognisable product was obtained from the attempted reduction of the ester by the Clemmensen and the Huang-Minlon procedure.

4 : 5-*Bishydroxymethylphenanthrene* (IV).—A mixture of powdered lithium aluminium hydride (8 g.), the methyl ester (III) (2·5 g.), and dry ether (200 c.c.) was heated under reflux for 30 minutes. The cooled reaction mixture was cautiously decomposed with ice and dilute sulphuric acid. Evaporation of the dried (Na_2SO_4) ethereal layer and crystallisation from benzene furnished the diol (2·25 g.) as needles, m. p. 152—159°. Recrystallisation from the same solvent effected little improvement in the wide melting range of the product (cf. Newman and Whitehouse, *loc. cit.*); possibly the azeotropic dehydrating effect of boiling benzene caused some conversion into the cyclic ether (V). A sharply melting specimen, m. p. 171—172°, was obtained by crystallisation from alcohol and heating the crystalline alcoholate thus obtained (Found : C, 80·6; H, 5·9. Calc. for $C_{16}H_{14}O_2$: C, 80·7; H, 5·9%). The *diacetate*, prepared by heating the diol with acetic anhydride and potassium acetate, crystallised from light petroleum (b. p. 100—120°) in prisms, m. p. 105° (Found : C, 74·6; H, 5·75. $C_{20}H_{18}O_4$ requires C, 74·55; H, 5·6%).

Cyclic Ether (V).—The above diol (1 g.) was dissolved in benzene (10 c.c.), a small quantity of anhydrous calcium chloride added, and the solution saturated with dry hydrogen chloride. Filtration, evaporation of the benzene, and crystallisation of the residue from light petroleum (b. p. 60—80°) gave an almost quantitative yield of the cyclic ether (V) as plates, m. p. 77—78° (Found : C, 87·3; H, 5·4. Calc. for $C_{16}H_{12}O$: C, 87·3; H, 5·5%). The 2 : 4 : 7-trinitrofluorenone *complex* (Orchin and Woolfolk, *J. Amer. Chem. Soc.*, 1946, **68**, 1727) crystallised in orange prisms, m. p. 190—191°, from alcohol (Found : N, 7·7. $C_{29}H_{17}O_8N_3$ requires N, 7·9%).

4 : 5-*Bisbromomethylphenanthrene* (VI).—4 : 5-Bishydroxymethylphenanthrene (280 mg.), benzene (20 c.c.), and pyridine (10 mg.) were treated with phosphorus tribromide (600 mg.), and the mixture was warmed to 50° for 2 hours. The benzene solution was then washed with water and sodium hydrogen carbonate solution, dried (Na_2SO_4), and evaporated. The residue of 4 : 5-*bisbromomethylphenanthrene* (370 mg., 85%) crystallised from benzene in prisms, m. p. 194° (decomp.) (Found : C, 52·6; H, 3·45; Br, 43·9. $C_{16}H_{12}Br_2$ requires C, 52·8; H, 3·3; Br, 43·8%).

Attempted reduction of (VI). (*a*) The bisbromomethyl compound (50 mg.), dissolved in acetone (10 c.c.), was shaken in an atmosphere of hydrogen with palladium–strontium carbonate catalyst (50 mg.; 2%). Removal of catalyst and solvent yielded a low-melting solid which was purified by sublimation at 10^{-3} mm. to give prisms, m. p. 75—76° undepressed on admixture with the cyclic ether (V). (*b*) 4 : 5-Bisbromomethylphenanthrene (500 mg.) was dissolved in benzene (20 c.c.) and slowly added to a boiling solution of lithium aluminium hydride (2 g.) in ether (250 c.c.) (cf. Johnson *et al.*, *J. Amer. Chem. Soc.*, 1948, **70**, 3738). The solution was heated under reflux for 16 hours and carefully decomposed with ice and dilute sulphuric acid. Evaporation of the dried (Na_2SO_4) ethereal layer furnished a solid which sublimed readily at 70°/10^{-3} mm. giving prisms, m. p. 75—76° undepressed on admixture with the cyclic ether (V).

*Di*iso*thiuronium Dibromide* (VII).—A solution of 4 : 5-bisbromomethylphenanthrene (100 mg.) and thiourea (64 mg.) in dry acetone (10 c.c.) was heated under reflux for 30 minutes. The precipitated white solid (136 mg., 96%) was filtered off and washed with a little acetone; it consisted of the *dibromide* (VII) in practically pure condition, m. p. 200—201°. Crystallisation from alcohol–acetone gave rosettes of needles, m. p. 200—201° (Found : C, 41·9; H, 4·0. $C_{18}H_{20}N_4Br_2S_2$ requires C, 42·0; H, 3·9%).

4 : 5-*Dimethylphenanthrene* (VIII).—A solution of the di*iso*thiuronium dibromide (340 mg.) in alcohol (15 c.c.) was heated under reflux with Raney nickel (*ca.* 500 mg.) for 1 hour. Removal of catalyst and solvent gave a low-melting solid which was dissolved in light petroleum (b. p. 40—60°) and chromatographed over alumina. The movement of the sharp band formed was easily followed by means of its intense blue fluorescence in ultra-violet light. Development of the chromatogram with light petroleum washed the band through the column; evaporation of the solvent and crystallisation of the solid thus obtained from methanol gave 4 : 5-dimethylphenanthrene (150 mg., 76%) as prisms, m. p. 75—76° (Found: C, 93·4; H, 6·8. Calc. for $C_{16}H_{14}$: C, 93·2; H, 6·8%). The 2 : 4 : 7-trinitrofluorenone complex crystallised from alcohol in scarlet needles, m. p. 120—121° (Found: N, 7·9. Calc. for $C_{29}H_{19}O_7N_3$: N, 8·1%). Fission of this complex by chromatography in benzene over alumina gave the parent hydrocarbon with m. p. identical with the sample obtained as above. The picrate, m. p. 109—110°, formed orange prisms from alcohol (Found : N, 9·75. Calc. for $C_{22}H_{17}O_7N_3$: N, 9·7%).

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