503. *Alkylation of the Aromatic Nucleus. Part IV.* Phenanthrene.*

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Cyclohexyl benzenesulphonate decomposes thermally in phenanthrene to give a mixture of four isomeric cyclohexylphenanthrenes which have been identified, and their proportions estimated.

s-Butyl benzenesulphonate similarly gives a mixture of isomeric s-butylphenanthrenes.

Alkylation of an aromatic system by the thermal decomposition of an alkyl sulphonate is an electrophilic substitution involving a carbonium ion. A characteristic of this alkylation for toluene is that the proportion of *meta*-isomer is much greater than is obtained in other electrophilic substitutions.[1] It is obviously desirable that information should be obtained with other systems. Some results are already available for naphthalene, and we now record a study of the alkylation of phenanthrene designed to determine what isomers are formed and the relative amount of each.

The most complete results have been obtained for thermal decomposition of cyclohexyl benzenesulphonate in fused phenanthrene. A mixture of isomeric cyclohexylphenanthrenes was obtained, and from it, 9-, 1-, and 2-cyclohexylphenanthrenes were isolated pure and identified by comparison with authentic specimens. A fourth isomer was also isolated, purified through its picrate, and characterised by its quinone. There is strong presumptive evidence that it is 3-cyclohexylphenanthrene. This is provided by comparison with the product of the thermal decomposition of s-butyl benzenesulphonate in phenanthrene. 9-, 3-, and 2-s-Butylphenanthrenes have been recognised as components of the mixture, and the ratio of 3- to 2-isomer is of the same order as in the cyclohexyl series. Further, when the product of each alkylation is oxidised by chromic acid, the 3-substituted phenanthraquinone is the most readily isolated. A less forceful argument is that substitution in the 4-position is not likely to be extensive for steric reasons; indeed, the only reliable report of substitution in the 4-position is in nitration, and then the 4-nitro-compound is present only to the extent of 6% of the mononitration product.

Estimation of the relative amounts of isomeric cyclohexylphenanthrenes in the alkylation product was made by comparison of the infrared spectra of the mixture and of each of the pure isomers. The composition of the alkylation product is given in the Table. For comparison the composition of the mononitration product of phenanthrene is also given.

	Percentage of isomer:				
Substituent	1-	2-	3-	4-	9-
Cyclohexyl-	15	17·5	27·5	—	35
Nitro-	26	7	22	6	36

A significant feature of these results is that the differences between the proportion of the isomers formed in alkylation are not as great as might be expected from an electrophilic substitution nor are they in the order predicted.[2] When toluene is alkylated by the thermal decomposition of the alkyl sulphonates, there is also much less difference between the proportions of the three possible isomers than would be expected; the product contains a relatively high proportion of the *meta*-isomer. This has also been observed when toluene is alkylated by alkyl halides under the influence of gallium bromide and similar promoters in conditions which do not bring about isomerisation.[2] It is suggested by Brown and Nelson [2] that this random orientation in alkylation may be due to the high reactivity of

* Part III, preceding paper.

[1] (*a*) Hickinbottom and Rogers, *J.*, 1957, 4124; (*b*) Brown and Nelson, *J. Amer. Chem. Soc.*, 1953, **75**, 6292.

[2] (*a*) Dewar and Warford, *J.*, 1956, 3570; (*b*) Dewar and Bavin, *ibid.*, p. 167.

the attacking species; its consequent low selectivity does not permit any great differentiation between attack at the *meta*- and *para*-positions. If this hypothesis is applied to phenanthrene, it follows that the distribution of the isomers expected on a theoretical basis will be modified in the direction of reducing the differences in the proportions of isomers formed. These conclusions are borne out by our work and are strongly supported by observations on naphthalene which show that a mixture of 60% of α- and 40% of 2-cyclohexylnaphthalene is formed by the thermal decomposition of cyclohexyl benzenesulphonate in naphthalene; with s-butyl the mixture contains 88% of 1- and 12% of 2-butylnaphthalene. Benzyl benzenesulphonate gives mainly the 1-isomer. It is clear that the nature of the substituting alkyl group has a marked influence on the proportion of 1- and 2-isomers in the alkylation of naphthalene. The most satisfactory explanation so far is Brown and Nelson's.

Experimental

Preparation of 1-*Cyclohexylphenanthrene.*—A solution of 1,2,3,4-tetrahydro-1-oxophenanthrene (2·5 g.) (Haworth [3]) in benzene (15 c.c.) was added to an ice-cold solution of cyclohexyl-lithium (from cyclohexyl bromide, 8·1 g.) in light petroleum. The mixture was heated under reflux for 4 hr., then kept at room temperature for 12 hr. before being added to aqueous sulphuric acid. The product, taken up in ether was distilled up to 53°/0·5 mm. to remove solvent and the more volatile products. The residue was purified by three crystallisations from alcohol and consisted of 1-cyclohexyl-3,4-dihydrophenanthrene, m. p. 100—102° (yield 0·13 g.). By heating this with selenium (0·05 g.) at 320° for 9 hr., 1-*cyclohexylphenanthrene* was obtained, as white needles, m. p. 121·5—123°, from alcohol (Found: C, 91·9; H, 8·0. $C_{20}H_{20}$ requires C, 92·3; H 7·7%). The picrate, m. p. 142—143°, formed yellow crystals.

Preparation of 9-*Cyclohexylphenanthrene.*—To a Grignard reagent from 9-bromophenanthrene (87 g.) in ether–benzene solution, was added cyclohexanone (24·5 g.) in dry ether. The product, after removal of magnesium salts, was refluxed with an excess of acetic anhydride for 10 hr., and the anhydride and acetic acid were then distilled off. 9-Cyclohexenylphenanthrene crystallised. It was purified by crystallisation from benzene–ethyl alcohol, and had m. p. 126·5—128° (yield 42 g.) (Found: C, 92·8; H, 7·3. Calc. for $C_{20}H_{18}$: C, 93·0; H, 7·0%) (Bergmann and Bergmann [4] give m. p. 132°). It was hydrogenated in ethyl acetate (Raney nickel, 3 atm.) to 9-*cyclohexylphenanthrene*, small sparkling tablets, m. p. 112—113° from alcohol (Found: C, 92·1; H, 7·5. $C_{20}H_{20}$ requires C, 92·3; H, 7·7%); the picrate formed orange needles, m. p. 152—153°, from alcohol.

Attempts to prepare 3-cyclohexylphenanthrene from 3-bromophenanthrene by using the corresponding Grignard or lithium compound were unsuccessful. Similarly, the preparation of 4-cyclohexylphenanthrene from 1,2,3,4-tetrahydro-4-oxophenanthrene was unsuccessful.

Preparation of 2-*s-Butylphenanthrene.*—2-Acetylphenanthrene (Mosettig [5]) (9·5 g.) in benzene (175 c.c.) was added to ethylmagnesium bromide (from magnesium, 2·2 g.). The mixture was kept overnight, refluxed for 2 hr., then poured into an excess of dilute hydrochloric acid. When the solvent was removed from the washed and dried organic layer, there remained a brown solid (8·1 g.) from which 2-*s-butenylphenanthrene* was obtained as light brown plates, m. p. 116—117° (from alcohol) (Found: C, 93·4; H, 6·6. $C_{18}H_{16}$ requires C, 93·1; H, 6·9%). It was characterised as the picrate, buff-yellow needles, m. p. 94—96°, from alcohol. Hydrogenation of 2-s-butenylphenanthrene in alcohol (Pd–C, 3 atm.) gave 2-*s-butylphenanthrene*, white needles, m. p. 44·5—45·5° (Found: C, 92·2; H, 7·7. $C_{18}H_{18}$ requires C, 92·3; H, 7·7%). It gave a yellow picrate, m. p. 116—117°, from alcohol.

Preparation of 3-*s-Butylphenanthrene.*—3-*s-Butenylphenanthrene* was similarly prepared from 3-acetylphenanthrene (Mosettig [5]). It is a viscous liquid, b. p. 172—181°/0·9 mm., n_D^{20} 1·6848—1·6880 (Found: C, 92·7; H, 6·9%), characterised by its orange picrate, m. p. 95—96°. 3-*s-Butylphenanthrene*, from hydrogenation of the olefin, is a viscous liquid, b. p. 166—169°/1·5 mm., n_D^{20} 1·6418 (Found: C, 92·4; H, 7·7%); picrate, m. p. 126—130°.

[3] Haworth, *J.*, 1932, 1129.
[4] Bergmann and Bergmann, *J. Amer. Chem. Soc.*, 1937, **59**, 1443.
[5] Mosettig and van de Kamp, *ibid.*, 1930, **52**, 3704.

Oxidation of 3-s-butylphenanthrene in acetic acid by chromic acid gave the *quinone*, pale orange-coloured needles, m. p. 151—152·5° (Found: C, 82·2; H, 6·3. $C_{18}H_{16}O_2$ requires C, 81·8; H, 6·1%).

Reaction of Phenanthrene with Cyclohexyl Benzenesulphonate.—A mixture of phenanthrene (200 g.) and the sulphonate (100 g.) was stirred and kept at 115° for 5 hr., an exothermic reaction temporarily raising the temperature to 145°. The product was worked up to give a mixture of cyclohexylphenanthrenes (A), b. p. 192—216°/0·7 mm. (yield 52 g.), and a higher-boiling fraction (13·7 g.), b. p. 216—260°/0·7 mm., a yellow glass from which no solid was isolated. There remained, undistilled, a dark brown glass (11·6 g.) not further examined.

9-Cyclohexylphenanthrene could be isolated from fraction A by crystallisation from alcohol. Oxidation of the reaction mixture by chromic acid in acetic acid solution gave 3-cyclohexylphenanthraquinone (see below). A more satisfactory separation was achieved by the slow evaporation of a solution of fraction A in light petroleum (b. p. <40°). Eight successive crops (nos. 1—8) of crystals were collected of approximately equal bulk. There remained a residue (B).

(a) 9-*Cyclohexylphenanthrene.* Repeated crystallisation (alcohol or other common solvent) of the first crop gave 9-cyclohexylphenanthrene, m. p. 113—113·5° (Found: C, 92·2; H, 7·7. Calc. for $C_{20}H_{20}$: C, 92·3; H, 7·7%); picrate, orange needles, m. p. 150—151°. These m. p.s were unchanged by admixture with authentic specimens. The identity of this hydrocarbon was confirmed by oxidising it by chromic acid in acetic acid to phenanthraquinone.

(b) 1-*Cyclohexylphenanthrene.* The mother-liquors from the first crystallisations of crop 1 were evaporated to dryness and the solid residue was crystallised from alcohol; 1-cyclohexylphenanthrene was obtained, m. p. and mixed m. p. 121·5—122·5° (Found: C, 92·2; H, 8·0%); picrate, m. p. and mixed m. p. 142—144°.

(c) 2-*Cyclohexylphenanthrene.* Crystallisation of crops 4 and 5 gave 2-cyclohexylphenanthrene, m. p. 113—113·5° (Found: C, 91·8; H, 8·0%); picrate, yellow needles, m. p. 147—148·5°. This was heated with selenium at 330° for 3 days, whereby 2-phenylphenanthrene, m. p. 198·5—200°, was obtained (Found: C, 94·1; H, 5·5. Calc. for $C_{20}H_{14}$: C, 94·5; H, 5·5%); the 1 : 3 : 5-trinitrobenzene adduct formed yellow needles, m. p. 157—158°, from benzene. Oxidation by chromic acid in acetic acid gave a quinone as small red needles, m. p. 222—223° (with previous softening) (from chloroform–alcohol) (Found: C, 84·3; H, 5·4. Calc. for $C_{20}H_{12}O_2$: C, 84·5; H, 4·3%) [Newman [6] gives 2-phenylphenanthrene, m. p. 196·6—197·2°; 1 : 3 : 5-trinitrobenzene adduct, yellow needles, m. p. 156·4—157·4°; quinone, deep red needles, m. p. 220—221° (decomp.)].

(d) 3-*Cyclohexylphenanthrene.* The residue (B) (above) was freed from solvent, and converted, in alcoholic solution, into picrate. By repeated crystallisation and separation, a pale orange-coloured picrate, m. p. 154—156° was obtained; the m. p. was depressed by admixture with the picrates of the other cyclohexylphenanthrenes which had been isolated. A benzene solution of the picrate, passed through activated alumina, gave 3-cyclohexylphenanthrene as a viscous oil. It was characterised by oxidation by chromic acid in acetic acid to 3-*cyclohexylphenanthraquinone*, m. p. 218—219° (Found: C, 82·5; H, 6·5. $C_{20}H_{18}O_2$ requires C, 82·7; H, 6·3%); this was identical with the quinone isolated from the oxidation of the mixture of cyclohexylphenanthraquinones from the alkylation.

Reaction of Phenanthrene with s-Butyl Benzenesulphonate.—The benzenesulphonate (75 g.) and phenanthrene (200 g.) were fused and stirred at 130°. After ½ hr., the mixture darkened and there was a vigorous evolution of but-2-ene. The reaction was completed by keeping it at 130° for 2 hr.; the mixture was then cooled, taken up in ether–benzene (1·5 l.), washed with aqueous alkali, dried, and distilled to remove solvent and the excess of phenanthrene. The remainder boiled mainly between 170° and 176°/1·2 mm., n_D^{20} 1·6488 (19·4 g.), and consisted of s-butylphenanthrenes. A further distillation concentrated the product into the range 160—162°/0·8 mm., n_D^{20} 1·6480 (Found: C, 92·3; H, 7·7. Calc. for $C_{18}H_{18}$: C, 92·3; H, 7·7%).

No crystalline picrate was obtained from this mixture. Oxidation by chromic acid in acetic acid gave a mixture of quinones, from which by draining on filter aids and crystallisation from alcohol, from acetic acid, and again from alcohol, 3-s-butylphenanthraquinone was obtained as orange needles, m. p. 151·5—153° not depressed by admixture with an authentic sample (Found: C, 81·3; H, 6·1. Calc. for $C_{18}H_{16}O_2$: C, 81·8; H, 6·1%).

The first alcoholic mother-liquors from the crystallisation of this quinone were evaporated

[6] Newman, *J. Org. Chem.*, 1944, **9**, 518.

to dryness and triturated with ether. Crystallisation of the residue from alcohol gave phenanthraquinone, m. p. 208—210° not depressed on admixture with an authentic sample.

It was estimated spectroscopically that not more than 12% of the 3-isomer is present in the mixture and not more than 6% of the 2-isomer. The presence of 9-s-butylphenanthrene is inferred from oxidation by chromic acid in acetic acid to phenanthraquinone.

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