31. *Electrophilic Substitution. Part I. Preliminary Investigations.*

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This paper describes the first stages in a programme designed to provide quantitative data on the reactivity of aromatic systems in electrophilic substitutions. Preliminary investigations of the nitrations of phenanthrene, triphenylene, and pyrene are described. The work of Schmidt and Heinle[1] on the nitration of phenanthrene is criticised.

ONE of us[2] recently developed a simplified molecular-orbital (MO) treatment of chemical problems which seems to represent an advance over existing theories. Not only does it offer a complete justification for the qualitative electronic theory of organic chemistry which Lapworth, Robinson, Ingold, and others have developed, but it allows in principle simple quantitative estimates of the relations between structure and chemical reactivity. It is therefore a matter of some importance to test this aspect of the new theory, and we have initiated a programme designed to provide suitable quantitative data.

Since the treatment is based on the transition-state theory, it is necessary to select a reaction for which the transition state is likely to have a simple and known configuration. Aromatic substitution reactions form an obvious example, for it has been known[3] for some time that their rates can be interpreted in terms of a simple model for the transition state. The MO treatment can be applied most unambiguously to the reactions of hydrocarbons, and substitution in aromatic hydrocarbons is therefore a particularly suitable reaction; the more so since neither the classical electronic theory, nor the resonance theory, can predict the relative reactivities of different hydrocarbons, although they can be used (in a rather dubious manner) to estimate the relative reactivities of the different positions in a given hydrocarbon.

The treatment can be applied very simply to substitution in aromatic hydrocarbons, by using Wheland's model for the transition state. The activation energy ΔE should then be given[2] by:

$$\Delta E = C_x - 2\beta(a_{or} + a_{os}) \equiv C_x - \beta N_t \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where C_x is a constant characteristic of the reagent X, β is the carbon–carbon resonance integral, and a_{or}, a_{os} are the coefficients of the atomic orbitals of atoms adjacent to that (t) at which reaction takes place in the non-bonding molecular orbital of the transition state. The quantity $N_t \equiv 2(a_{or} + a_{os})$ is therefore a direct measure of the relative reactivity of a given position in a given hydrocarbon, reactivity being greater the smaller N_t is. N_t may be termed the "reactivity number" of atom t. The coefficients can be found very simply, even in large polycyclic systems.

It has been shown[2,4] that the available evidence is in good general agreement with equation (1); in particular, since equation (1) holds regardless of the reagent, orientation in hydrocarbons should be the same for reagents of all types (electrophilic, nucleophilic, and radical); and this appears to be the case. A particularly striking confirmation is provided by recent measurements[5] of the relative rates of reaction of a wide range of hydrocarbons with methyl radicals. If it can be assumed that entropy effects are negligible, and that reaction occurs at one position in each hydrocarbon, it follows from equation (1) that

$$RT \log k/k_0 = -\beta\,(N^\circ - N_t) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where k_0 is the velocity constant and N° reactivity number for substitution in benzene, and k and N_t the corresponding quantities for substitution at the most reactive position in some other hydrocarbon. The Table shows that the experimental results for methylation follow equation (2) closely. Strictly, one should correct the experimental results for

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[1] Schmidt and Heinle, *Ber.*, 1911, **44**, 1448.
[2] Dewar, *J. Amer. Chem. Soc.*, 1952, **74**, 2341 *et seq.*
[3] Wheland, *J. Amer. Chem. Soc.*, 1942, **64**, 900.
[4] Bavin, Thesis, London, 1955.
[5] Levy and Szwarc, *J. Amer. Chem. Soc.*, 1955, **77**, 1949.

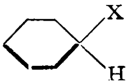
statistical factors, and the theoretical predictions for the fact that two or more positions in a hydrocarbon often have similar reactivity numbers; but these corrections would be small in comparison with the enormous range (10,000 : 1) of variation in the observed velocity constants. The rates of trichloromethylation of hydrocarbons by trichloromethyl radicals [6] must also follow equation (2), since Levy and Szwarc [5] have shown that the rates of methylation and trichloromethylation run parallel.

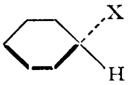
Comparison of observed and predicted reactivities for methylation of hydrocarbons.

Hydrocarbon	$\log k/k_0$	$N^\circ - N_t$	$(\log k/k_0)/(N_0 - N_{rs})$
Diphenyl	0·70	0·24	2·9
Naphthalene	1·34	0·50	2·7
Phenanthrene	1·43	0·51	2·8
Chrysene	1·76	0·64	2·8
Pyrene	2·10	0·80	2·6
Stilbene	2·26	0·80	2·8
Benzanthracene	2·67	0·96	2·8
Anthracene	2·91	1·04	2·8
Naphthacene	3·97	1·28	3·1

Although the new theory therefore seems to account quantitatively for the relative rates of radical substitution in hydrocarbons there is one disturbing feature. The value of the parameter β calculated from equation (2) and the data tabulated is too small (4·7 kcal., instead of ~20 kcal. required in calculations of conjugation energies). A similar difficulty has been known for some time to exist for naphthalene, where Wheland's calculations [3] implied that the α : β ratio in substitution should be very much greater than that observed. An obvious and likely explanation [7] would be that the structures (I) considered by Wheland are not transition states but stable intermediates; the transition states are of the type (II), where the reagent X is still remote and weakly bound.

(I)





(II)

This would mean that the quantity ΔE in equation (1) is a heat of reaction and not an activation energy; and that the k's in equation (2) are equilibrium constants and not velocity constants. The success of the preceding treatment would then imply the existence of a linear relation between activation energy and heat of reaction—a common and familiar phenomenon.

Suppose that the energy of activation (ΔE) and the heat of reaction (ΔH) for substitution by a given reagent X are connected by such a linear relation, so that

$$\Delta E = A_x + B_x \Delta H \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where A_x and B_x are constants characteristic of X. Then equations (1) and (2) become:

$$\begin{aligned}\Delta E &= A_x + B_x C_x - 2\beta B_x (a_{or} + a_{os}) \\ &= C_x' - 2\beta_x(a_{or} + a_{os}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)\end{aligned}$$

$$\boldsymbol{R}T \log k/k_0 = -\beta_x(N^\circ - N_t) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where

$$\beta_x = \beta B_x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Therefore equation (2) will apply quite generally if the linear relation (3) holds, except in that β must now be regarded, not as a universal constant, but as a parameter characteristic of a given substitution reaction. As long as the reagent and the reaction conditions remain the same, β_x will remain constant; otherwise it may vary.

It is evident from equation (6) that, the smaller β_x is, the smaller will be the difference in reactivity between two different positions in a given hydrocarbon, and so the smaller the selectivity of orientation shown by the reagent X. This agrees well with the conclusions

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[6] Kooyman and Farenhorst, *Trans. Faraday Soc.*, 1953, **49**, 58.
[7] Cf. Brown, *Quart. Rev.*, 1952, **6**, 63.

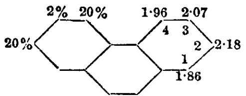
reached by Brown and his collaborators [8] concerning the selective effects of substituents on orientation; a highly reactive reagent will presumably be one for which β_x is small and such a reagent should show low selectivity. Their investigations show clearly the existence of linear relations between activation energies for substitution by different reagents and so provide indirect evidence for the relation indicated in equation (2). Brown and Nelson [9] expressed the view that transition states in electrophilic substitutions do not conform to the Wheland model, but involve less disturbance of the π-electrons in the substrate; our argument supports this view.

Although the available data on electrophilic substitution are in good general agreement with equation (2), there are some anomalies. Sulphonation and the Friedel–Crafts reaction commonly give " abnormal " products. In sulphonation these are known to arise only when the substitution becomes reversible, so that the proportions of isomers are determined by the thermodynamic equilibrium between them rather than by their rates of formation. The same is probably true of the Friedel–Crafts reaction.[10] Any valid test of equation (1) must be based on reactions which are definitely irreversible, such as nitration and halogenation.

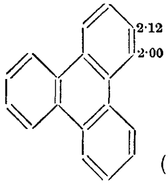
We have obtained evidence in support of Gore's [10] suggestion by showing that 9-acetylphenanthrene is the main product when phenanthrene is acetylated under conditions where the intermediate complex is precipitated and so removed from further reaction; acetylation under homogeneous conditions, in nitrobenzene, gives a mixture of the 2- and the 3-isomer.[11]

The nitration of phenanthrene does, however, seem to proceed in a manner very dissimilar to that predicted. Schmidt and Heinle [1] studied this reaction in great detail; they separated the mixture of mononitrophenanthrenes by laborious fractional crystallisation and reported that the proportions of isomers were those shown in (III). These are in qualitative disagreement with the relative reactivities predicted from the reactivity numbers [also shown in (III)]. In particular, they stated that they could find no trace of the 1-isomer, despite a careful search; the 1-position is predicted to be second in order of reactivity, and to be only a little less reactive than the 9-position.

We have re-examined the nitration of phenanthrene in hot acetic acid, following the procedure of Schmidt and Heinle. The product was a dark uncrystallisable gum and contained large quantities of coloured materials strongly adsorbed on alumina (probably quinones and polynitro-compounds). It is therefore evident that the percentage composition given by Schmidt and Heinle must have been based on the total weight of pure isomers isolated and not on the weight of the crude product; since the separation of these isomers, even by chromatography, is exceedingly difficult, the yields of pure isomers obtained by them by simple fractional crystallisation were probably small. Further, the identities of the materials described by them as 2- and 4-nitrophenanthrene are in doubt; [12] their materials were at best impure and may even have been mixtures or solid solutions containing little of the isomers claimed. Schmidt and Heinle's results cannot therefore be regarded as reliable, or as evidence against the order of reactivities predicted theoretically.



(III)



(IV)

We have nitrated phenanthrene, using a large excess of the hydrocarbon in acetic anhydride and working at low temperatures. Under these conditions the product is a yellow crystalline mixture of mononitrophenanthrenes, containing only traces of quinones

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[8] Brown and co-workers, *J. Amer. Chem. Soc.*, 1955, **77**, 2300, 2306, 2310, 3037.

[9] Brown and Nelson, *ibid.*, 1953, **75**, 6592.

[10] Gore, personal communication; cf. *Chem. Rev.*, 1955, **55**, 229.

[11] Mosettig and van de Kamp, *J. Amer. Chem. Soc.*, 1930, **52**, 3704.

[12] Bavin and Dewar, *J.*, 1955, 4477.

or polynitro-compounds. Chromatography proved unsuccessful for quantitative separation, but we were able to isolate 1-nitrophenanthrene for the first time.[13] We were at first misled as to the proportion of this isomer in the mixture, believing it to be very small; subsequent examination has indicated that it is in fact a major component. This has been confirmed by Mr. E. W. T. Warford (unpublished work) who has shown by isotope dilution analysis that it forms almost one-third of the nitration product.

We have also studied the nitration of triphenylene. The only information in the literature concerning orientation referred to Friedel–Crafts reactions and sulphonation, which give 2-substitution, whereas the reactivity numbers shown in (IV) indicate that the 1-position should be somewhat the more reactive. Nitration of triphenylene, under the conditions used for phenanthrene, gave almost exclusively a mixture of mononitrotriphenylenes; previously only a trinitrotriphenylene, of unknown structure, had been described.[14] The mixture of 1- and 2-nitrotriphenylene, m. p. 169° and m. p. 165—166°, respectively, was separated by chromatography. These were oriented by reduction to the aminotriphenylenes and conversion into the two fluorotriphenylenes. Authentic 2-aminotriphenylene was prepared from 2-acetyltriphenylene [15] by Beckmann rearrangement of the oxime to 2-acetamidotriphenylene followed by hydrolysis. Authentic 2-fluorotriphenylene was prepared by the Rapson synthesis [16] from *p*-bromofluorobenzene and *cyclo*hexenyl*cyclo*hexane. The ratio of isomers in the nitration product is estimated to be 1·0 : 1·0 ± 0·1.

Since substitution in the 1-position of triphenylene must be subject to severe steric hindrance, this result implies that the 1-position is intrinsically the more reactive, as predicted.

In nitration of pyrene under similar conditions we find that 1-nitropyrene is almost the sole product; no evidence could be found for the formation of any other mononitropyrene. This is surprising, for although the 1-position should be the most reactive, the difference between the reactivity numbers for 1- and 4-substitution is less than that between the numbers for α- and β-substitution in naphthalene, where the ratio of isomers formed on nitration is only * about 10 : 1. We are confident that the ratio is very much greater than this in the case of pyrene.

In conclusion, we have shown that nitration of aromatic hydrocarbons proceeds cleanly under suitable conditions, giving almost exclusively mixtures of mononitro-derivatives; it is therefore an ideal reaction for quantitative studies of reactivity. We have also shown that previous work on the nitration of phenanthrene is unreliable and that there is no evidence that the predictions of molecular-orbital theory in this case are incorrect; and we have shown that the nitration of triphenylene conforms qualitatively with prediction.

EXPERIMENTAL

Purification of Phenanthrene.—Phenanthrene was purified by boiling with maleic anhydride in xylene, followed by crystallisation from acetic acid. It formed colourless plates, m. p. 100° (lit., 100°), and the absorption spectrum was identical with that reported.[18]

Nitration of Phenanthrene.—(*a*) Nitration of phenanthrene by the method of Schmidt and Heinle,[1] with a slight excess of nitric acid in hot glacial acetic acid, gave a dark resin which appeared to contain large quantities of oxidation and polynitration products. (*b*) Phenanthrene (5 g.) in acetic anhydride (100 ml.) was treated at 10° with a solution of fuming nitric acid (0·25 equiv.) in acetic anhydride (4 ml.). Next day the yellow solution was poured into dilute sulphuric acid and crushed ice, and organic material extracted with benzene (5 × 100 ml.). After being washed with water, sodium carbonate solution, and again water, the solution was

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* Fierz-David and Sponagel [17] report a ratio of 20 : 1; we have, in a preliminary investigation, found values in the range 11—16 : 1.

[13] *Idem*, *Chem. and Ind.*, 1953, 543.
[14] Mannich, *Ber.*, 1907, **40**, 160.
[15] Buu-Hoï and Jacquignon, *J.*, 1953, 941.
[16] Rapson, *J.*, 1941, 15.
[17] Fierz-David and Sponagel, *Helv. Chim. Acta*, 1943, **26**, 98.
[18] Friedel and Orchin," Ultraviolet Spectra of Aromatic Compounds," Wiley and Sons, New York, 1941, No. 341.

evaporated, and the residue chromatographed from light petroleum on alumina (6 × 50 cm.). Phenanthrene (4·2 g.) was eluted in the first 15 l. After 250 l. of eluant had passed through the column, elution was continued with light petroleum containing benzene (2%), and fractions (500 ml. each) were collected. Most of the recovered materials melted over wide ranges and pure isomers were isolated only in a few cases. The isomers when isolated were identified by mixed m. p.s and ultraviolet absorption spectra with synthetic specimens.[12] Fraction 5 on recrystallisation first from methanol, then from acetic acid, gave 3-nitrophenanthrene, m. p. 173—174°. Fraction 6 also gave 3-nitrophenanthrene; recrystallisation (from light petroleum) of the material contained in the mother-liquors gave 1-nitrophenanthrene, m. p. 133—134°. Fraction 12 on recrystallisation from light petroleum gave 1-nitrophenanthrene; 9-nitrophenanthrene, m. p. 116°, was isolated from the mother-liquors by crystallisation from acetic acid. Fractions 13—21 consisted mainly of 9-nitrophenanthrene, m. p. 114—116° after recrystallisation from acetic acid. Fraction 22 after several crystallisations from methanol had m. p. 114—116°, strongly depressed by 9-nitrophenanthrene, scarcely depressed by 2-nitrophenanthrene; the ultraviolet absorption spectrum resembled that of 2-nitrophenanthrene.

It appears that 1- and 9-nitrophenanthrene are major components, the former appearing in fractions 5—12, the latter in fractions 12—21, also that quantitative separation of the mixture by chromatography would present a very difficult problem.

Acetylation of Phenanthrene.—A solution of pure phenanthrene (20 g.) in carbon disulphide (150 ml.) was cooled to 0°. Freshly distilled acetyl chloride (12·2 g., 1·4 mol.) was then added, followed by powdered aluminium chloride (35 g.). After ½ hour's stirring at 0° the mixture was left overnight at room temperature. Next day the complex was decomposed with ice and hydrochloric acid, the carbon disulphide distilled off, and the residual red oil isolated with carbon tetrachloride and fractionated. Mixed acetylphenanthrenes (16 g.) were collected at 260—280°/15 mm. Crystallisation from methanol containing a little acetone gave 2-acetylphenanthrene (0·35 g.), m. p. and mixed m. p. 140—142°. The hot mother-liquors were diluted with an equal volume of hot water and gave sticky needles, m. p. 60—70°, depressed by 3-acetylphenanthrene. Oxidation of this crude material (A) with hypochlorite gave an acid which was esterified in chloroform with diazomethane; after chromatography from light petroleum on alumina the methyl ester crystallised from light petroleum in colourless needles, m. p. 114—115°, undepressed by methyl 9-phenanthroate.[19] The yield of ester, based on (A), was 74%; (A) was therefore impure 9-acetylphenanthrene.

Nitration of Triphenylene.—Triphenylene [16] was purified by chromatography from light petroleum on alumina followed by crystallisation from benzene; it had m. p. 198—199°. Purified triphenylene (12 g.) in acetic anhydride (1500 ml.) was nitrated at 25° with acetyl nitrate (0·5 mol.). Next day the solution was poured into crushed ice and dilute sulphuric acid, and the product isolated with chloroform and chromatographed from light petroleum on alumina. After all the unchanged triphenylene (5·1 g.) had been eluted, elution was continued with light petroleum–benzene (5 : 1), giving a mixture of mononitrotriphenylenes (6·68 g.). Only traces of other materials remained on the column. The mixed mononitrotriphenylenes were rechromatographed and fractions collected: fraction 1, trace of triphenylene; fractions 2—6 (A), yellow prisms, m. p. 164—169° (2·91 g.); fraction 7, poorly formed crystals, m. p. 140—151° (0·52 g.); fractions 8—11 (B_1), yellow needles, m. p. 162—165° (1·12 g.); fractions 12—19 (B_2), yellow needles, m. p. 148—164° (1·9 g.). Crystallisation of fractions (A) from toluene gave yellow prisms, m. p. 169°, of 1-*nitrotriphenylene* (Found: C, 79·3; H, 4·1; N, 4·9. $C_{18}H_{11}O_2N$ requires C, 79·1; H, 4·1; N, 5·1%). Crystallisation of fractions (B_1) from toluene and then from acetic acid gave pale yellow needles, m. p. 165—166°, of 2-*nitrotriphenylene* (Found: C, 79·0; H, 4·2; N, 5·2%). Fraction (7) was shown by thermal analysis to be a mixture of about 60% of 1- and 40% of 2-nitrotriphenylene. Fractions (B_2) were shown by recrystallisation to be essentially impure 2-nitronaphthylamine.

1-*Aminotriphenylene.*—Reduction of 1-nitrotriphenylene (0·4 g.) with hydrazine and Raney nickel gave 1-*aminotriphenylene*, yellow needles (from toluene), m. p. 104—105° (Found: C, 88·2; H, 5·45; N, 5·75. $C_{18}H_{13}N$ requires C, 88·9; H, 5·4; N, 5·8%), not identical with 2-aminotriphenylene. The N-*acetyl derivative* crystallised from toluene in colourless needles, m. p. 252° (Found: N, 4·9. $C_{20}H_{15}ON$ requires N, 4·9%). The *benzylidene derivative* crystallised from alcohol in pale yellow needles, m. p. 140—140·5° (Found: N, 4·2. $C_{25}H_{17}N$ requires N, 4·2%). Solutions of the amine in hydrocarbon solvents showed an intense fluorescence.

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[19] Pschorr, *Ber.*, 1896, **29**, 496.

1-*Fluorotriphenylene.*—The nitro-compound (1·4 g.) was reduced and the crude amine diazotised and converted into the diazonium fluoroborate. This was decomposed by boiling it for 30 min. in light petroleum (b. p. 100—120°), and the resulting solution chromatographed on alumina. The highly fluorescent 1-*fluorotriphenylene* was eluted first, and crystallised from toluene in yellowish needles, m. p. 173—174°, raised by vacuum-sublimation and recrystallisation to 174—175° (Found : C, 87·9; H, 4·7. $C_{18}H_{11}F$ requires C, 87·8; H, 4·5%). The compound was shown to differ from 2-fluorotriphenylene, by mixed m. p. and comparison of the spectra.

1-p-*Fluorophenyl*-2-cyclo*hexenyl*cyclo*hexanol.*—To a Grignard reagent prepared from *p*-bromofluorobenzene (87·5 g.) and magnesium (13·5 g.) was added slowly 2-*cyclo*hexenyl*cyclo*hexanone (90 g.), and the solution was left overnight. Isolation of the *alcohol* in the usual way gave an oil (79 g., 58%), b. p. 160—164°/1·5 mm., $n_D^{20.5}$ 1·5400, which solidified and then crystallised from light petroleum in prisms, m. p. 42—45° (Found : C, 79·1; H, 8·4. $C_{18}H_{23}OF$ requires C, 78·8; H, 8·4%).

2-*Fluoro*-5 : 6 : 7 : 8 : 9 : 10 : 11 : 12-*octahydrotriphenylene.*—The alcohol (32·5 g.) in carbon disulphide (100 ml.) was added to a suspension of powdered aluminium chloride (32 g.) in carbon disulphide (100 ml.) at 0°. After 1 hr. the mixture was left at room temperature. Next day water was added and the hydrocarbon isolated through its picrate (orange needles, m. p. 180°, from benzene or alcohol). After decomposition of the picrate with alumina in the usual way, 2-*fluoro-octahydrotriphenylene* was obtained as a white solid which crystallised from alcohol in needles, m. p. 146—147° (Found : C, 84·8; H, 7·5. $C_{18}H_{19}F$ requires C, 85·0; H, 7·5%).

2-*Fluorotriphenylene.*—Dehydrogenation of the octahydro-derivative over palladised charcoal at 310—335° gave 2-*fluorotriphenylene*, in almost theoretical yield, crystallising from light petroleum in colourless needles, m. p. 185—185·5° (Found : C, 88·3; H, 4·8%).

2-*Acetamidotriphenylene.*—2-Acetyltriphenylene [15] (1·6 g.) was converted into its oxime with hydroxylamine hydrochloride (1 g.) in pyridine (5 ml.) and ethanol (7 ml.), and the crude oxime (m. p. 190—196°) treated with phosphorus pentachloride (1·2 g.) in benzene (30 ml.), then boiled under reflux for 15 min. Water was added and the *acetamidotriphenylene* collected; it crystallised from methanol in colourless needles (0·7 g.), m. p. 260—261° (Found : C, 84·0; H, 5·4; N, 5·05. $C_{20}H_{15}ON$ requires C, 84·2; H, 5·3; N, 4·9%).

2-*Aminotriphenylene.*—The acetyl derivative (300 mg.) was boiled under reflux for 36 hr. with hydrochloric acid (5 ml.) in ethanol (200 ml.). The *amine*, isolated by evaporation and basification, crystallised from light petroleum in pale yellow blades, m. p. 139—140° (Found : C, 89·0; H, 5·7; N, 5·9. $C_{18}H_{13}N$ requires C, 88·9; H, 5·4; N, 5·8%).

Orientation of 2-*Nitrotriphenylene.*—Reduction of 2-nitrotriphenylene with hydrazine and Raney nickel gave 2-aminotriphenylene, crystallising from light petroleum in colourless blades, m. p. and mixed m. p. 142—143°. The amine was converted, as for the 1-isomer, into 2-fluorotriphenylene which crystallised from toluene in needles, m. p. 181—182°, raised to 182—183° by recrystallisation from light petroleum, mixed m. p. with synthetic 2-fluorotriphenylene 184—185°.

Nitration of Pyrene.—Pyrene was purified by chromatography from benzene–light petroleum (1 : 1) on alumina, forming rhombohedral plates, m. p. 153—154° (lit., 156°). Pure pyrene (10 g.) in acetic anhydride (250 ml.) was nitrated at room temperature with a solution of 95% nitric acid (2 ml.) in acetic anhydride (3 ml.). Next day the solution was poured into dilute sulphuric acid and crushed ice, and the precipitate recrystallised from methanol and then from acetic acid, giving orange-yellow needles (5·1 g.) of 1-nitropyrene, m. p. 155° (lit., 153—154°). Concentration of the mother-liquors gave a further 2·9 g., m. p. 146—148°. Dilution of the filtrate with water gave a solid (1·9 g.) which was chromatographed from light petroleum on alumina. After a trace of pyrene, more 1-nitropyrene was collected (1·2 g.); the remaining material, which was highly coloured and strongly adsorbed, probably consisted of dinitropyrenes. Repeated chromatography failed to yield any isomers in the 1-nitropyrene fractions.

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