37. *The Reactions of Pyrene with Free Radicals and with Sodium.*

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Pyrene reacts with free benzyl and phenyl radicals at the 1-position, *i.e.* that of its highest free-valence number, displaying a reactivity much lower than that of anthracene. Its sodium adduct, however, which has been previously shown to react with carbon dioxide principally at the 4-position, also reacts with benzyl chloride at the 4-position. The difference between the radical reaction and that of the sodium adduct is discussed. The syntheses of several substituted pyrenes are described.

We have now extended a study of the actions of benzyl[1,2] and phenyl[3] radicals on polycyclic aromatic compounds to pyrene. This hydrocarbon was of interest since its marked inhibiting effect on the autoxidation of benzaldehyde[4] catalysed by benzoyl peroxide is at variance with its low maximum free-valency number $F_{\max}$ in the four equivalent positions 1, 3, 6, and 8,[5] and with its moderate methyl radical affinity,[6] though not so greatly at variance with the polarographic half-wave potential[7] or with the electron localisation energy at the 1-position as computed by Dewar.[8]

Theoretical calculations for pyrene are less certain than those for anthracene and phenanthrene derivatives on account of assumptions concerning the electron localisation at the two inner carbon atoms that carry no hydrogen atom. For instance, the uncoupled structure (I) in which the periphery of the molecule retains its complete conjugation may be significant in the reaction between sodium and pyrene.[9] *X*-Ray measurements[10]

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[1] Beckwith and Waters, *J.*, 1957, 1001.

[2] Waters and Watson, *J.*, 1957, 253.

[3] Norman and Waters, *J.*, 1958, 167.

[4] Dunn, Waters, and Roitt, *J.*, 1954, 580.

[5] Berthier, Coulson, Greenwood, and Pullman, *Compt. rend.*, 1948, **226**, 1906.

[6] Levy and Szwarc, *J. Amer. Chem. Soc.*, 1955, **77**, 1949.

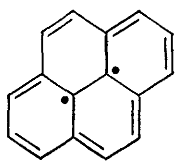
[7] Bergman, *Trans. Faraday Soc.*, 1954, **50**, 829.

[8] Dewar, *J. Amer. Chem. Soc.*, 1952, **74**, 3357.

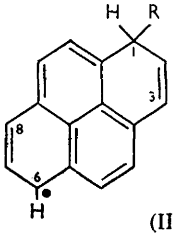
[9] Neunhoefer and Woggon, *Annalen*, 1956, **600**, 34.

[10] J. M. Robertson, " Organic Crystals and Molecules," Cornell University Press, 1953, p. 200.

indicate that this inner carbon–carbon bond has a much lower bond order than the average for the other bonds in the molecule. Furthermore, measurements of the free-radical, or electron reactivity of pyrene have not hitherto been supported by isolation and identification of products. The object of this work was to determine the points of free-radical, and of electron, attack on pyrene; it has shown that correlations between measurements of chemical reactivity and theoretical calculations concerning the structure of pyrene cannot be uniformly related because different reaction mechanisms can be involved.



(I)



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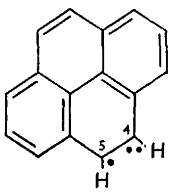

(III)

From our work only a comparative estimate of the reactivity of pyrene towards free radicals can be obtained. Whereas reaction of anthracene with benzyl radicals is complete, pyrene is attacked only slightly, and this difference accords well with its lower methyl-radical affinity. The much more reactive phenyl radical gives higher yields of substituted product, as would be expected.

By allowing pyrene to react for two weeks with benzyl radicals in large excess,[1] from decomposing *tert.*-butyl peroxide in boiling toluene, a 3·4% yield of 1-benzylpyrene was obtained and 75% of pyrene recovered. This indicates that benzyl radicals attack, as in structure (II) (the odd electron being distributed between position 6 and others in the molecule), at the carbon atom having the highest $F_{\max}$ and the lowest electron localisation energy. Similarly, from the reaction of pyrene with phenyl radicals, produced by the action of zinc powder on a suspension of benzenediazonium·zincichloride $(PhN_2)_2ZnCl_4$, in dry acetone,[3] 1-phenylpyrene was obtained together with traces of diphenylpyrenes, probably the 1 : 6- and the 1 : 8-compound. The structures of these 1-substituted pyrenes have been established by relation to the work of Vollmann, Becker, Corell, and Streeck [11] who prepared 1-benzoylpyrene and converted it *via* 1 : 6-dibenzoylpyrene into pyranthrone and by the direct conversion of 1-aminopyrene into 1-phenylpyrene. We have reduced 1-benzoylpyrene directly to the 1-benzylpyrene obtained by the action of benzyl radicals on pyrene, and converted 1-nitropyrene into 1-aminopyrene and thence into pyrene-1-diazonium fluoroborate which when decomposed in benzene in the presence of sodium acetate yielded 1-phenylpyrene, identical with the product of direct phenylation.

Neunhoefer and Woggon [9] obtained 4 : 5-dihydropyrene from the sodium adduct of pyrene and ammonium bromide in liquid ammonia, and by treating the adduct, prepared in an ethereal solution of ammonia, with carbon dioxide they obtained pyrene-4-carboxylic acid as expected if the adduct had the electron-localised structure (III).[9] From the adduct and benzyl chloride, in ether, we obtained 4-benzylpyrene, and have confirmed this structure by making the same compound from pyrene-4-carboxylic acid. A trace of a dibenzylpyrene was also obtained. This, from spectral evidence, appears to be 4 : 9-dibenzylpyrene; it is not 4 : 5-dibenzylpyrene, which we have synthesised unambiguously from pyrene-4 : 5-quinone. The proof of the structure of pyrene-4-carboxylic acid also depends on a sequence relating it to pyrene-4 : 5-quinone.[9] The infrared spectra of these pyrene derivatives, listed below, give further support to these orientations. The ultra-violet spectra are all characteristically of pyrene type.

Establishment of the these structures shows clearly that whilst the electrically neutral free radicals, benzyl and phenyl, attack pyrene at the point of maximum free valence, sodium gives up an electron to pyrene to form a radical-anion which, on the approach of a cationoid reagent such as carbon dioxide or benzyl chloride, reacts as if the added electron were localised mainly at the carbon–carbon bond of highest bond order, as in structure (III).

It seems therefore that single-electron and neutral free-radical addition to aromatic systems are dissimilar processes and consequently that polarographic redox potentials of aromatic compounds need not be consistent with radical affinities. As yet, however, experimental disagreements with wide theoretical approximations of this type are so few that examples such as the reactivity of pyrene described above, deserve note.

EXPERIMENTAL

Attack of Benzyl Radicals on Pyrene.—Pyrene (6 g.), *tert.*-butyl peroxide (7 g.), and toluene (250 ml.) were refluxed under nitrogen for 2 weeks, more peroxide being added after the first week. After removal of steam-volatile products the residue was chromatographed (Al_2O_3, type H), giving pyrene (4·5 g.) and a yellow gum that darkened in sunlight. Sublimation at 170°/0·02 mm. and crystallisation from methanol gave crystals (0·3 g.), m. p. 89°, identical (mixed m. p., replicate ultraviolet and infrared spectra) with authentic 1-benzylpyrene (see below).

Attack of Sodium and then Benzyl Chloride on Pyrene.—Pyrene (5 g.) in ether (150 ml.) was added to sodium in liquid ammonia (100 ml.), and the ammonia allowed to evaporate slowly in nitrogen. Dry benzyl chloride was then added cautiously until the solution was decolorised. After addition of alcohol, solvents were evaporated, volatile material was removed by steam distillation, and the residue was chromatographed on alumina. It yielded pyrene (2·9 g.), 4-*benzylpyrene*, m. p. 170° (0·12 g.) (Found: C, 94·1; H, 5·7. $C_{23}H_{16}$ requires C, 94·5; H, 5·5%), and a much smaller amount of a white solid, m. p. 222—224°, probably impure 4 : 9-dibenzylpyrene (Found: C, 93·2; H, 5·1. $C_{30}H_{22}$ requires C, 94·2; H, 5·8%).

Attack of Phenyl Radicals on Pyrene.—Benzenediazonium zincichloride (28·0 g., 4 mol.) was suspended in dry acetone (200 ml.) in which was dissolved pyrene (3·37 g., 1 mol.); a little chalk was added to ensure neutrality. The mixture, kept in purified dry nitrogen, was stirred vigorously and zinc powder (" AnalaR "; 5 g.) was added in small portions. When the initial reaction had subsided, the mixture was refluxed for 1 hr.; a test with " H " acid was then negative. The solution was filtered, the solvent removed by evaporation, and the residue extracted with light petroleum (b. p. 60—80°). Chromatography of this solution (Al_2O_3, type H) yielded, in order: diphenyl (30 mg.), m. p. 72°, pyrene (1·38 g.; 41%), 1-*phenylpyrene* (1·0 g., 21%), m. p. 84° (from methanol) (Found: C, 94·4; H, 5·1. $C_{22}H_{14}$ requires C, 94·9; H, 5·1%), and a mixture of two compounds, separated by fractional crystallisation from ethanol [Found, in compound (*a*), m. p. 209° (0·03 g.): C, 94·8; H, 5·1. In compound (*b*), m. p. 215° (0·04 g.): C, 94·3; H, 5·1. $C_{28}H_{18}$ requires C, 94·9; H, 5·1%].

Syntheses of Reference Compounds.—1-*Benzylpyrene.* Aluminium chloride (2·5 g.) was added gradually to a stirred solution of pyrene (2·5 g.) and benzoyl chloride (1·9 g.) in benzene (25 ml.). After an hour water was added and the mixture distilled in steam. Material extracted from the residue by benzene gave 1-benzoylpyrene (2·4 g.), m. p. 126° (from ethanol); Vollmann *et al.*[11] give 127°. This ketone (2·4 g.) was reduced during 5 hr. by hydrazine hydrate (78% w/w; 1 ml.) and potassium hydroxide (1 g.) in refluxing diethylene glycol (20 ml.), the temperature being kept at 220—240° for the last 3 hr. The mixture was poured into water and extracted with ether, giving 1-benzylpyrene (1·8 g.), m. p. 89° (from methanol) (Found: C, 94·5; H, 5·3. Calc. for $C_{23}H_{16}$: C, 94·5; H, 5·5%): Buu-Hoï, Eckert, and Demerseman [12] give m. p. 91°.

1 : 6- *and* 1 : 8-*Dibenzylpyrene.* Pyrene (5 g.) was condensed with an excess of benzoyl chloride, as described by Vollmann *et al.*,[11] and the resulting mixture of 1 : 6-dibenzoylpyrene (1·2 g.), m. p. 237° (lit. 239°), and 1 : 8-dibenzoylpyrene (2·4 g.), m. p. 159—163° (lit. 165°), was separated by crystallisation from acetic acid. Each of these compounds was reduced as described above, and purified chromatographically. 1 : 6-*Dibenzylpyrene* had m. p. 194° (Found: C, 93·8; H, 6·0. $C_{30}H_{22}$ requires C, 94·2; H, 5·8%); 1 : 8-dibenzylpyrene which was not rigorously purified had m. p. 184—188°.

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[11] Vollmann, Becker, Corell, and Streeck, *Annalen*, 1937, **531**, 1.

[12] Buu-Hoï, Eckert, and Demerseman, *J. Org. Chem.*, 1954, **19**, 726.

4 : 5-*Dibenzylpyrene.* Pyrene was oxidised with ozone and the resulting 4-formylphenanthrene-5-carboxylic acid was converted into pyrene-4 : 5-quinone (yellow needles; m. p. 307°; lit. 310°) as described by Vollmann *et al.*[11] The quinone (2 g.) in hot dry benzene (500 ml.) was added to the Grignard reagent from benzyl chloride (7 g.) in ether (200 ml.), and the mixture was boiled for 3 hr. The organic product after chromatography gave a mixture (1·2 g.) of the stereoisomers of 4 : 5-dibenzyl-4 : 5-dihydro-4 : 5-dihydroxypyrene, m. p. 105—115°, which was isomerised during 3 hr. by refluxing thionyl chloride, giving 5 : 5-*dibenzyl*-4 : 5-*dihydro*-4-*oxopyrene* (1 g.), m. p. 164° (from light petroleum) (Found: C, 90·6; H, 5·8. $C_{30}H_{22}O$ requires C, 90·5; H, 5·6%). Its spectrum showed ketonic absorption at 5·98 μ. The ketone (150 mg.) was reduced with a large excess of lithium aluminium hydride in ether to the corresponding secondary alcohol which, without purification, was treated with sulphuric acid (0·5 ml.) in acetic acid (10 ml.) to effect the retropinacol shift to 4 : 5-*dibenzylpyrene* (95 mg.), m. p. 158° (from methanol) (Found: C, 94·1; H, 5·9. $C_{30}H_{22}$ requires C, 94·2; H, 5·8%).

4-*Benzylpyrene.* Pyrene (5 g.) in ether (100 ml.) was added to sodium (1·2 g.) in liquid ammonia (100 ml.) under nitrogen, and the ammonia was allowed to evaporate slowly. Carbon dioxide was passed into the red mixture until the deep colour had disappeared. Pyrene-4-carboxylic acid was extracted from the product with aqueous potassium carbonate, precipitated with hydrochloric acid and purified by sublimation at 200°/0·02 mm.; the yield was 1·5 g. (m. p. 256—257°; Neunhoefer and Woggon [9] give 258°). A suspension of the acid (1 g.) in benzene (30 ml.) was refluxed for 30 min. with phosphorus pentachloride (1 equiv.), then aluminium chloride (1·2 g.) was added and the mixture was refluxed for a further 30 min. The resulting benzene solution was washed with water and alkali, then passed through alumina, giving a yellow ketonic (infrared spectrum) gum (0·8 g.) which was reduced with hydrazine and alkali as described for the isomer (above). The resulting 4-*benzylpyrene* (0·4 g.), m. p. 170°, was purified chromatographically; it was identical with the substance obtained by the action of benzyl chloride on the sodium adduct of pyrene.

4-*Benzyl*-sym-*hexahydropyrene and* 4 : 9-*dibenzyl*-sym-*hexahydropyrene.* Pyrene was reduced to *sym*-hexahydropyrene, m. p. 131—132°, with sodium in boiling pentyl alcohol and this was converted into 4-benzoylhexahydropyrene, m. p. 109° (lit. 109°) by the usual procedure.[11] Reduction with hydrazine and alkali, followed by chromatography and crystallisation from methanol, gave 4-*benzyl*-1 : 2 : 3 : 6 : 7 : 8-*hexahydropyrene*, m. p. 65° (Found: C, 92·4; H, 7·4. $C_{23}H_{22}$ requires C, 92·6; H, 7·4%). Treatment of hexahydropyrene with a larger amount of benzoyl chloride gave the 4 : 9-dibenzoylhexahydropyrene, m. p. 272—273° (lit. 273°),[11] which by similar reduction gave 4 : 9-*dibenzyl*-1 : 2 : 3 : 6 : 7 : 8-*hexahydropyrene*, m. p. 211° (from ethanol) (Found: C, 92·4; H, 7·2. $C_{30}H_{28}$ requires C, 92·7; H, 7·3%). Attempted dehydrogenation of these mono- and di-benzoyl- and -benzyl-hexahydropyrenes was unsuccessful.

1-*Phenylpyrene.* 1-Nitropyrene [13] was reduced with palladium–charcoal and hydrazine hydrate in ethanol to 1-aminopyrene, m. p. 117°.[14] To a solution of the diazotised amine was added an excess of saturated aqueous sodium fluoroborate. The precipitated pyrene-1-diazonium fluoroborate was washed with water, ethanol, and finally benzene. The salt (1 g.) was suspended in dry benzene (10 ml.) and anhydrous sodium acetate (0·3 g.) and acetic anhydride (0·1 g.) were added. After 24 hr. at room temperature, during which there was slow evolution of nitrogen, the mixture was refluxed for 2 hr. Water was added, the organic layer dried ($CaCl_2$), the solvent removed by evaporation, and the residue, in light petroleum (b. p. 60—80°), was passed through alumina. 1-*Phenylpyrene* was obtained as plates, m. p. 84°, in 24% yield (Found: C, 94·6; H, 5·1. $C_{22}H_{14}$ requires C, 94·9; H, 5·1%).

Infrared Spectra.—Diphenylpyrenes. Compound (*a*), m. p. 209°, and compound (*b*), m. p. 215°, both showed strong bands corresponding to a monosubstituted benzene, (*a*) at 13·08 and 14·44 μ, (*b*) at 13·08 and 14·20 μ. Each had an intense band corresponding to two adjacent hydrogen atoms in an aromatic system, (*a*) at 11·94 and (*b*) at 11·88 μ. Neither showed any absorption in the range 12·35—13·45 μ which would indicate three adjacent aromatic hydrogen atoms, whereas the spectrum of pyrene itself has a band of medium strength at 13·40 μ, corresponding to its two pairs of three adjacent hydrogen atoms.

Ultraviolet Spectra.—Details are given in the Table.

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[13] Bavin and Dewar, *J.*, 1956, 164.

[14] Dewar and Mole, *J.*, 1956, 2556.

Ultraviolet spectra [wavelength in Å (log $\varepsilon_{\text{max.}}$ in parentheses)].

Pyrene	—	2400 (4·9)	2640 (4·3)	2750 (4·7)	3190 (4·5)	3350 (4·7)
1-Benzylpyrene	—	2430 (4·8)	2655 (4·4)	2765 (4·7)	3265 (4·4)	3430 (4·6)
4-Benzylpyrene	—	2440 (4·7)	2670 (4·3)	2780 (4·7)	3280 (4·3)	3450 (4·5)
1 : 6-Dibenzylpyrene	—	2450 (4·1)	2680 (3·7)	2790 (4·0)	3340 (3·8)	3500 (4·0)
?4 : 9-Dibenzylpyrene	—	2450 (4·8)	2670 (4·45)	2780 (4·7)	3240 (4·4)	3400 (4·6)
4 : 5-Dibenzylpyrene	—	2450 (4·8)	2670 (4·5)	2780 (4·8)	3260 (4·4)	3420 (4·6)
1-Phenylpyrene	—	2440 (4·8)	2670 (4·5)	2770 (4·7)	—	3400 (4·5)
Diphenylpyrenes:						
(*a*) m. p. 209°	2020 (4·8)	2400 (4·8)	—	2770 (4·7)	—	3420 (4·6)
(*b*) m. p. 215°	2040 (4·8)	2480 (4·7)	2720 (4·5)	2820 (4·7)	—	3510 (4·6)
1 : 2 : 3 : 6 : 7 : 8-Hexahydropyrene	—	2340 (4·8)	2960 (4·0)	—	—	—
4-Benzylhexahydropyrene	—	2380 (4·9)	2980 (4·0)	—	—	—

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