509. *The Action of Benzoyl Peroxide on Polycyclic Aromatic Hydrocarbons.*

By Ivan M. Roitt and William A. Waters

When acted upon by benzoyl peroxide at 80° in chlorobenzene, under nitrogen, anthracene, 1 : 2-benzanthracene, and 3 : 4-benzopyrene are attacked in their exposed *meso*-positions and benzoate groups (Ph•CO•O) are substituted for hydrogen. Phenanthrene and chrysene are inert under these conditions, whilst 1 : 2-5 : 6-dibenzanthracene reacts only if there is access of air, dibenzanthraquinones then being formed in low yield.

The relative order of reactivities, *i.e.*, 3 : 4-benzopyrene $\gg$ anthracene, 1 : 2-benzanthracene > 1 : 2-5 : 6-dibenzanthracene > phenanthrene, chrysene, follows the order of the " free valence numbers " of the reacting positions, though it is also possible that steric hindrance may be responsible for discrimination in the point of attack on 1 : 2-benzanthracene and for the lack of reactivity of 1 : 2-5 : 6-dibenzanthracene under an inert atmosphere.

Under similar conditions 9-methylanthracene is very reactive. It yields 1 : 2-di-9′-anthranylethane, two dimers of this substance which are thought to be related structurally to dianthracene, 9-benzoyloxy-10-methylanthracene, and the 10′-benzoyloxy-derivative of 1 : 2-di-9′-anthranylethane.

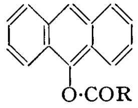
The experimental results are discussed in relation both to concepts of homolytic reactivity and to previously known chemical and biochemical oxidations of these hydrocarbons.

One of the most intriguing features of the biological oxidation of aromatic hydrocarbons is the observation that they can be attacked in positions which are different from those affected by the majority of the oxidising or substituting agents in regular laboratory use, and it has been suggested, tentatively, that this biochemical oxidation, which is essentially a hydroxylation, might perhaps be due to hydroxyl, or similar, free radicals (see *Biochem. Soc. Symposia*, 1950, No. 5). We have therefore attempted to discover whether the free-radical reactions of polycyclic aromatic hydrocarbons resemble at all the distinctive biochemical reactions.

Our earlier attempt in this connection—to affect oxidations of biological type by the use of perbenzoic acid—failed (*J.*, 1949, 3060) and at about that time it was realised (Derbyshire and Waters, *Nature*, 1950, **165**, 401; Swern, *J. Amer. Chem. Soc.*, 1947, **69**, 1692) that the per-acids were reagents of heterolytic type which oxidised by release of cationoid hydroxyl groups :

$$\mathrm{Ac{-}O{-}OH} + \mathrm{H{-}Ar} \longrightarrow \mathrm{Ac{-}O{-}H} + \mathrm{HO{-}Ar}$$

Recent conceptions (Criegee, *Annalen*, 1948, **560**, 133; Rigby, *J.*, 1950, 1907) of the mechanism of glycol fission throw doubt on the homolytic character of the oxidising action of lead tetra-acetate, especially in ionising solvents such as acetic acid, and consequently the studies by Fieser and Hershberg (*J. Amer. Chem. Soc.*, 1938, **60**, 1893, 2542) and Fieser and Putnam (*ibid.*, 1947, **69**, 1036, 1041) of the oxidation of polycyclic aromatic hydrocarbons may not be truly representative of their modes of attack by free radicals. These workers found that at 35—55° lead tetra-acetate effected addition of two acetate radicals to the *meso*-positions of anthracene. At higher temperatures subsequent elimination of acetic acid yielded 9-acetoxyanthracene (I; R = Me). 1 : 2-Benzanthracene and 3 : 4-benzo-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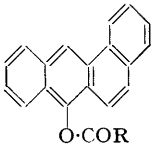
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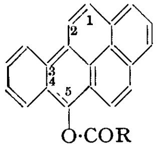
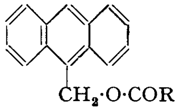


(III)

pyrene similarly yielded (II and III; R = Me), whereas 10-methyl-1 : 2-benzanthracene and 20-methylcholanthrene yielded products analogous to (IV) by attack on the reactive methyl, or methylene, groups. The latter products are strongly indicative of homolytic action.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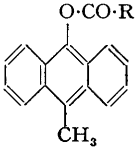

(V)

In order to study a reaction which would more certainly be of the free-radical type we have investigated the reactions between a number of polycyclic aromatic hydrocarbons and benzoyl peroxide in chlorobenzene solution at 80°. At this temperature benzoyl peroxide first dissociates into benzoate radicals ($Ph{\cdot}CO_2{\cdot}$) which then either dehydrogenate other molecules directly or attack them with (or after) loss of carbon dioxide so as to form phenyl derivatives. When solutions contain much more reactive substrates than chlorobenzene, then the benzoate radicals can be made to react exclusively as such, without loss of carbon dioxide. This is true for instance of solutions containing polymerizable olefins (Swain, Stockmayer, and Clarke, *ibid.*, 1950, **72**, 5426) or readily substituted aromatic compounds such as phenols (Cosgrove and Waters, *J.*, 1949, 3189; 1951, 388). Liberation of carbon dioxide therefore indicates degradation of benzoate radicals to phenyl radicals in the course of their reactions, whilst the production of benzoic acid indicates hydrogen abstraction by free benzoate radicals. Consequently the more reactions of free benzoate radicals as such are involved the less will be the evolution of carbon dioxide and to some degree the more the production of free benzoic acid. From the Table below it can be seen clearly that this trend follows the order of increasing reactivity in the hydrocarbons which have been examined.

Reaction of benzoyl peroxide with aromatic hydrocarbons in chlorobenzene solution at 80°

Substance	CO_2, % *	$Ph{\cdot}CO_2H$, % †	Hydrocarbon recovered, %	Other products
Chlorobenzene alone	66·2	—	—	Chlorodiphenyls and phenyl benzoate
	67·6	35·5	—	
Anthracene	11·9	44·6	11·2	9-Benzoyloxyanthracene Anthraquinone
1 : 2-Benzanthracene	14·7	43·6	24	10-Benzoyloxy-1 : 2-benzanthracene
1 : 2-5 : 6-Dibenzanthracene	38·9	40·1	89	As for control
	— (with O_2	47·7	31·5	Dibenzanthraquinones)
3 : 4-Benzopyrene	2·6	46·9	—	5-Benzoyloxy-3 : 4-benzopyrene
Phenanthrene	48·9	28	85	As for control
Chrysene	57·7	27·6	87	,,
9-Methylanthracene	2·3	52	None	1 : 2-Dianthranylethane, its dimers, 9-benzoyloxy-10-methylanthracene, etc.
	2·1	51·3	—	

* Calc. for $Ph{\cdot}CO{\cdot}O{-}O{\cdot}CO{\cdot}Ph \longrightarrow 2Ph{\cdot}CO_2{\cdot}$; $Ph{\cdot}CO_2{\cdot} \longrightarrow Ph{\cdot} + CO_2$.
† Calc. for $Ph{\cdot}CO{\cdot}O{-}O{\cdot}CO{\cdot}Ph \longrightarrow 2Ph{\cdot}CO_2{\cdot}$; $Ph{\cdot}CO_2{\cdot} + H{-}X \longrightarrow Ph{\cdot}CO_2{-}H$.

Equimolar solutions of hydrocarbon and benzoyl peroxide were used; the concentrations of the hydrocarbons differed according to their solubilities.

Benzoate radicals which are resonance-stabilised would be expected to be selective in their action and to react mainly with solute molecules at their most reactive positions, whilst the much more reactive phenyl radicals would be expected to attack all vicinal molecules, and in our dilute solutions of the sparingly soluble hydrocarbons this should lead almost exclusively to reaction with the solvent, though recent work indicates that even phenyl radicals react at decidedly different rates with different aromatic compounds (Augood, Hey, Nechvatal, Robinson, and Williams, *Research*, 1951, **4**, 386; Augood, Hey, and Williams, *J.*, 1952, in the press; Huisgen and Sorge, *Annalen*, 1950, **566**, 172).

We have in fact isolated benzoates from a number of the polycyclic hydrocarbons, but have not been able to isolate any phenyl derivatives : the presence of chlorodiphenyls has often been suspected though their isolation has not been undertaken. Actual isolation of products was difficult, so though pure compounds have been obtained by repeated chromatographic separation their yields cannot be taken as indicative of the relative reactivities of the hydrocarbons concerned. Nevertheless the natures of the products have been so clearly defined by comparative syntheses and by the use of both ultra-violet and infra-red spectra that it is now quite evident that attack on the higher polycyclic hydrocarbons by benzoate radicals does not resemble their biochemical hydroxylation but has much in common with lead tetra-acetate oxidation. For example, metabolic oxidation of 1 : 2-5 : 6-dibenzanthracene in rats and mice leads to the introduction of hydroxyl groups into the side rings in the 4′- and the 8′-position (Boyland, Levi, Mawson, and Roe, *Biochem. J.*, 1941, **35**, 184; Dobriner, Rhoads, and Lavin, *Proc. Soc. Exp. Biol. N.Y.*, 1939, **41**, 67); 1 : 2-benzanthracene is similarly attacked in the 4′-position (Berenblum and Schoental, *Cancer Res.*, 1943, **3**, 145, 686) and 3 : 4-benzopyrene in the 8-position (Berenblum, Crowfoot, Holiday, and Schoental, *ibid.*, p. 151); moreover, from the metabolic oxidation of anthracene it has been possible to isolate 1 : 2-dihydro-1 : 2-dihydroxyanthracene (Boyland and Levi, *Biochem. J.*, 1936, **30**, 728) and this has been ascribed to an initial process of free-radical addition.

On account of the behaviour of 1 : 2-5 : 6-dibenzanthracene (see below) it was found necessary to carry out all reactions in a stream of dry nitrogen, by means of which the carbon dioxide was removed as it was formed and could easily be collected and weighed. If air was allowed access then several of the reaction mixtures gave more complex products than those described below, and it may well be that the courses of the oxidation reactions of several of the polycyclic hydrocarbons can be influenced by the presence or absence of even small amounts of oxygen.

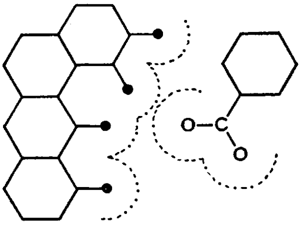
From anthracene which reacted to the extent of 90% with a molar proportion of benzoyl peroxide there was obtained a 15% yield of 9-benzoyloxyanthracene (I; R = Ph) and a little anthraquinone. Since the gummy residues could also be oxidised to anthraquinone with chromic acid it appears that attack is confined to the *meso*-positions. 1: 2-Benzanthracene was slightly less reactive and similarly yielded 10-benzoyloxy-1 : 2-benzanthracene (II; R = Ph) but no trace of the 9-substituted isomer. 1 : 2-5 : 6-Dibenzanthracene scarcely reacted under nitrogen, but if air was present some oxidation to 9 : 10-dibenzanthraquinone occurred. The resinous residue from this reaction, on dichromate oxidation in acetic acid, gave some benzoic acid and small amounts of both the 9 : 10(*meso*)- and the 3 : 4-("*K*")-dibenzanthraquinones. Direct measurements showed that benzoyl peroxide catalysed slow oxygen uptake by solutions of 1 : 2-5 : 6-dibenzanthracene in chlorobenzene; consequently the quinones must result from a secondary autoxidation process which is being investigated further. 3 : 4-Benzopyrene proved to be very reactive and gave a 33% yield of purified 5-benzoyloxy-3 : 4-benzopyrene (III; R = Ph), the identity of which was established by independent synthesis from 5-acetoxy-3 : 4-benzopyrene (Fieser and Hershberg, *J. Amer. Chem. Soc.*, 1939, **61**, 1565). In contrast, neither phenanthrene nor chrysene was attacked at all. Evidently the exposed *meso*-positions of anthracene derivatives are much more reactive than the "*K*" positions of phenanthrene derivatives towards free-radical attack, just as they are towards attack by polarised electrophilic reagents. The order of reactivity of these hydrocarbons, *viz.*, 3 : 4-benzopyrene $\gg$ anthracene, 1 : 2-benzanthracene $>$ 1 : 2-5 : 6-dibenzanthracene $>$ chrysene, phenanthrene, follows the order of the "free valence numbers" of their reacting positions (Burkitt, Coulson, and Longuet-Higgins, *Trans. Faraday Soc.*, 1951, **47**, 553; Kooyman and Farenhorst, *Nature*, 1952, **169**, 153).

Both the point of attack on 1 : 2-benzanthracene and the absence of attack on 1 : 2-5 : 6-dibenzanthracene in a nitrogen atmosphere deserve comment. Our results show replacement of hydrogen by a benzoate group. If a benzoate radical is to remove a hydrogen atom *directly* from a *meso*-position it will presumably attack linearly in the plane of the aromatic system, for this configuration gives the transition state of lowest activation energy for homolytic hydrogen transfer. Fig. 1 however shows that, owing to the positions of the angular benzenoid rings, the 10-position in 1 : 2-benzanthracene and both the 9- and the 10-position in 1 : 2-5 : 6-dibenzanthracene are sterically protected from attack in this way, though, clearly, these *meso*-positions are open to lateral attack upon the carbon centres by large atoms.

The favoured positions for attack on 1 : 2-5 : 6-dibenzanthracene may therefore depend not only upon relative "free valence numbers," or "electron densities," but also upon (i) the size of the attacking reagent and (ii) its direction of approach. Both the addition of free radicals to the *meso*-carbon atoms and the initial stage of any heterolytic substitution process follow the lateral route. Our results indicate either that steric hindrance is a cogent factor for our reaction or that the *meso*-positions of 1 : 2-5 : 6-dibenzanthracene are unexpectedly resistant to angular attack by benzoate radicals.

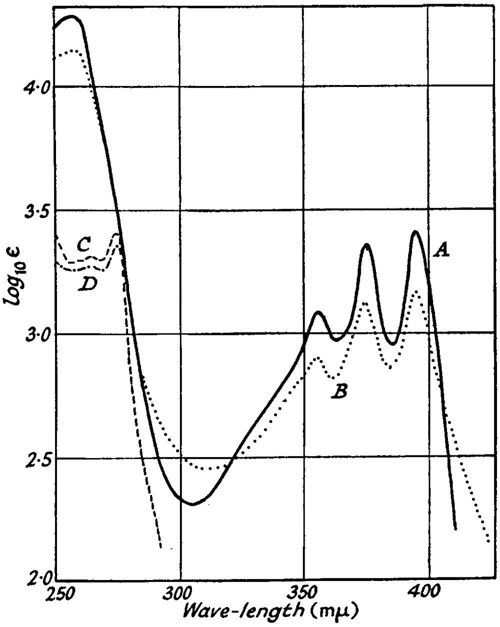
It may be noted that many free atoms and radicals, as for instance atomic chlorine, atomic bromine, and molecular oxygen, are known to be *added* to the carbon centres of aromatic nuclei, especially of the anthracene type. The *meso*-substitution products which we have isolated from the reactions with anthracene and 1 : 2-benzanthracene could conceivably result from the additions of benzoate radicals followed by the elimination of a molecule of benzoic acid.

FIG. 1. *Co-planar attack of a benzoate radical on 1 : 2-benzanthracene.*



The broken lines indicate the limiting van der Waals radii of interacting atoms. Attack on the *meso*-position is impeded by a hydrogen atom of the angular benzene ring.

FIG. 2. *Ultra-violet absorption spectra.*

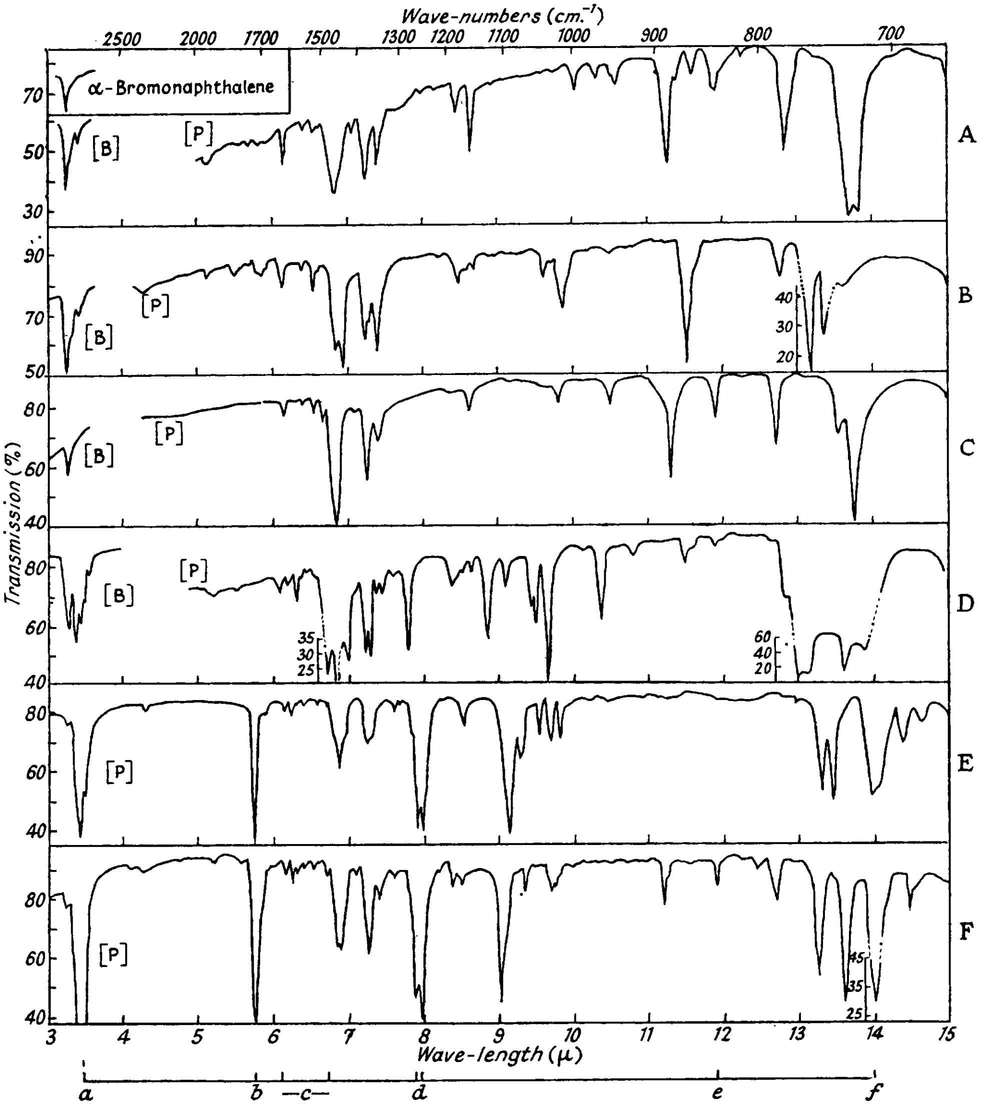


A, 1 : *2-Di-9'-anthranylethane.* *C, Product* D2.
B, Depolymerised D2. *D, Product* D1.

The foregoing work has been extended by the study of the reaction between benzoyl peroxide and 9-methylanthracene, a subject of some interest in view of the high carcinogenic activity of 9 : 10-dimethyl-1 : 2-benzanthracene. As judged by the negligible production of carbon dioxide, 9-methylanthracene reacts with all the free benzoate radicals as they are formed. It yields a number of reaction products; there was separated, first, a yellow fluorescent hydrocarbon, m. p. 310—315° (decomp.), identified as 1 : 2-di-9'-anthranylethane (VI; R = H) by its ultra-violet absorption spectrum (Fig. 2*A*) which showed the presence of a substituted anthracene ring system, and by its infra-red absorption spectrum (Fig. 3, *C*) which showed a distinctive maximum at 11·9 μ corresponding to the presence of a "lone" aromatic C–H group indicative of a single unsubstituted *meso*-position in an anthracene ring. Again the spectrum, in α-bromonaphthalene paste showed no absorption band at

3·42 μ such as would be expected for a methyl group. For confirmation the compound was synthesised from 10-methyleneanthrone by reduction with zinc dust in acetic–hydrochloric acid. Barnett and Matthews (*Ber.*, 1926, **59**, 768) who evidently obtained the same compound by following this route considered from their ultimate analyses that they had obtained the dihydro-derivative (VII). Our analyses of products from both preparative procedures give no support to this view, and the infra-red spectrum shows no similarity to that of 9 : 10-dihydro-9-methylanthracene (VIII) particularly in the region

FIG. 3. *Infra-red absorption spectra.*



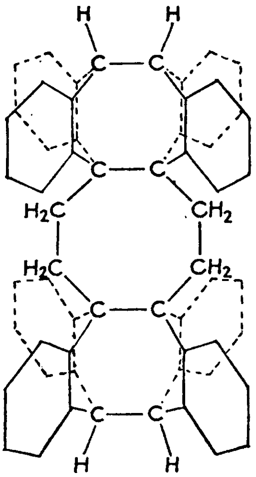
[*B*], Spectrum in α-bromonaphthalene paste.
[*P*], Spectrum in paraffin paste.
a, C—H stretching frequency in CH_3.
b, C═O stretching frequency.
c, C═C stretching frequencies.
d, —O—CO— bending frequencies.
e, " Out-of-plane " bending frequency of a " lone " aromatic C—H bond.
f, Bending frequencies of C—H bonds in an unsubstituted C_6H_5 group.

A, 9-Methylanthracene.
B, 10 : 10′-Dimethyl-9 : 9′-dianthranyl.
C, 1 : 2-Di-9′-anthranylethane.
D, 9 : 10-Dihydro-9-methylanthracene.
E, 9-Benzoyloxy-10-methylanthracene.
F, The 10-benzoyloxy-derivative of substance *C*.

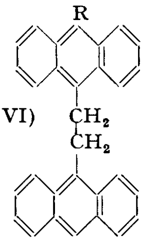
of 6·0—6·75 μ (indicative of stretching vibrations of C═C) in which there is close similarity between the spectra of (VI; R = H) and of 9-methylanthracene (see Fig. 3, *A* and *D*). For further structural verification we also prepared 10 : 10′-dimethyl-9 : 9′-dianthranyl (IX) by reducing 10-methylanthrone with zinc dust and ammonia (Barnett and Matthews, *loc. cit.*). It had a different melting point and its infra-red spectrum in α-bromonaphthalene paste showed the characteristic methyl group absorption maximum at 3·42 μ and the absence of the aromatic C–H absorption maximum at 11·9 μ.

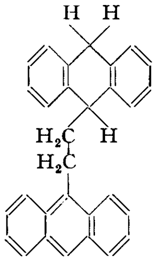
Together with (VI; R = H) were two colourless, non-fluorescent compounds of the same empirical formula as (VI; R = H); both had ultra-violet absorption spectra characteristic of benzenoid rings only. One of these (D1) separated slowly from toluene, giving crystals of two different forms, both of which softened at 270—280° and then became yellow though they did not melt until the decomposition temperature of (VI; R = H) was reached. The second substance (D2) gave crystals which melted almost completely at 230—236°, then resolidified, and finally decomposed at 278—284°. D1 and D2 had identical ultra-violet and almost identical infra-red spectra. When kept at 180° for 30 minutes in the polar solvent ethyl benzoate, D2 gave a yellow fluorescent solution having an ultra-violet absorption spectrum indicative of the presence of (VI; R = H), and, on irradiation of a solution of (VI; R = H) in benzene by ultra-violet light, some D1 was formed. Since D1 and D2 do not appear to possess the anthracene ring system we conclude that they are structurally related to dianthracene, the colourless photo-dimer of anthracene, though this substance itself possesses a much simpler infra-red spectrum than either D1 or D2. D1 and D2 may therefore be polymorphic crystalline modifications of the photo-dimer of 1 : 2-di-9′-anthranylethane, in which, as Fig. 4 shows, the two dianthracene portions are linked in a strainless 8-membered ring (the stereochemistry of such rings has been discussed by Baker, Banks, Lyon, and Mann, *J.*, 1945, 27). With both D1 and D2, dissociation, similar to that observed in ethyl benzoate solution, occurred when attempts were made to determine molecular weights in molten camphor by Rast's method.

FIG. 4.



(VI)





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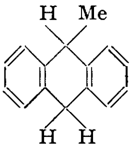

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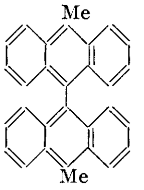
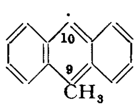


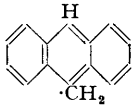
(IX)

The mother-liquors from these hydrocarbons contained 9-benzoyloxy-10-methylanthracene (V; R = Ph), which was also synthesised for comparison by benzoylation of 10-methylanthrone. There was also present the 10-benzoyloxy-derivative (VI; R = O·COPh) of dianthranylethane and a trace of anthraquinone. The isolation of the nuclear benzoate (V) and not the side-chain isomer (IV) is significant, for it indicates that although the *meso*-position 10 and the C–H bond of the methyl group in 9-methylanthracene can be attacked by benzoate radicals with comparable ease the nature of the succeeding reaction must be influenced considerably by the relative stabilities of the radicals (X) and (XI).

Resonance concepts indicate that (XI) should be much more stable than (X); it would therefore be more prone to persist and attain a concentration sufficient for dimerization. Nevertheless the formation of a little of the corresponding benzoate (IV; R = Ph) would have been expected. The formation of the dimers (VI) from (XI) accounts for the high yield of benzoic acid in this reaction. Our observations with 9-methylanthracene are analogous to those of Augood, Hey, and their colleagues (*loc. cit.*) who have recently shown that

(X)





(XI)

p-xylene and mesitylene yield dibenzyl derivatives of type (VI) on treatment with benzoyl peroxide, though toluene gave only methyldiphenyls. Again, these workers found no evidence of side-chain substitution by benzoate groups. Thus though the reactions of benzoyl peroxide with aromatic hydrocarbons exhibit many resemblances to those of lead tetra-acetate, studied by Fieser and his colleagues (*loc. cit.*), there are nevertheless some evident differences which may perhaps indicate different reaction mechanisms.

EXPERIMENTAL

Materials.—Anthracene was purified by Fieser's method ("Experiments in Organic Chemistry," D. C. Heath and Co., 1941, p. 345, footnote).

1 : 2-Benzanthracene was synthesised by cyclising the condensation product of naphthalene with phthalic anhydride and reducing the resulting 1 : 2-benzanthraquinone *via* 1 : 2-benzanthrone (Badger and Cook, *J.*, 1939, 804).

Commercial 1 : 2-5 : 6-dibenzanthracene (Messrs. L. Light & Co.) was purified by reaction with maleic anydride (Cook *et al.*, *Proc. Roy. Soc.*, 1932, *B*, **111**, 469) and crystallised to m. p. 261—262°.

Phenanthrene, chrysene, and 3 : 4-benzopyrene were commercial materials of satisfactory m. p.

9-Methylanthracene was prepared by the action of methylmagnesium bromide on anthrone in benzene (Sieglitz and Marx, *Ber.*, 1923, **56**, 1619) and purified to m. p. 80—81° by chromatography on alumina, followed by crystallisation from 96% ethanol.

Benzoyl peroxide was purified by dissolution in hot acetone, filtration into an equal volume of 80% ethanol, and finally drying over phosphoric oxide.

Chlorobenzene was purified by washing it with sodium hydroxide solution, drying, and fractional distillation.

For all chromatographic separations neutral alumina was prepared by stirring the commercial powder with an excess of warm dilute acetic acid for 30 minutes, washing the resulting solid very liberally with distilled water and then methanol, and finally reactivating it at 190°/4 mm. for 20 hours.

Unless otherwise stated, the reactions were carried out in chlorobenzene solution under a slow stream of purified nitrogen, and the carbon dioxide formed was determined by absorption in "Carbosorb." The reaction vessel was immersed in an oil-bath at 80° and shielded from direct sunlight. The reactions were allowed to proceed for 36 hours so as to ensure the complete decomposition of the benzoyl peroxide.

Reaction of Anthracene.—Anthracene (5·00 g., 0·028 mole) with benzoyl peroxide (6·75 g., 0·028 mole) yielded 0·291 g. (11·9%) of carbon dioxide. On cooling, the chlorobenzene solution was extracted 3 times with sodium hydrogen carbonate solution, then with water, and dried ($CaCl_2$). Acidification of the aqueous extract gave 3·01 g. (44·6%) of benzoic acid. The chlorobenzene solution after concentration to 15 c.c. and storage at 0° deposited a light yellow solid (0·38 g.) which after crystallisation from benzene proved to be unchanged anthracene (m. p. and mixed m. p. 212—214°). The chlorobenzene mother-liquor was evaporated to dryness and the resulting brown gum was chromatographed in a 10% solution of benzene in light petroleum (b. p. 60—80°) on neutralised activated alumina (150 g.). Elution (i) with the same mixture gave a semi-solid (0·51 g.) smelling of chlorodiphenyl which, on treatment with ether gave a further 0·18 g. of anthracene. Elution (ii) with 3 : 7 benzene–light petroleum gave a semi-solid (1·50 g.) which on treatment with ether gave a light yellow powder (0·95 g.), m. p. 167—170°. This crystallised from xylene–acetic acid in light yellow needles, m. p. 172—173° alone or mixed with an authentic specimen of 9-benzoyloxyanthracene (Barnett and Matthews, *J.*, 1923, **123**, 389) (Found: C, 84·3; H, 4·7. Calc. for $C_{21}H_{14}O_2$: C, 84·6; H, 4·7%). For further proof of structure, (*a*) hydrolysis with 50% sulphuric acid yielded benzoic acid, and (*b*) heating the substance (0·2 g.) for 4 hours with concentrated hydrochloric acid (8 c.c.) and ethanol (12 c.c.) and then pouring into water gave ethyl benzoate (identified by odour) and a precipitated solid; this was warmed with aqueous potassium hydroxide and the resulting solution was rapidly filtered into an excess of dilute hydrochloric acid, yielding anthrone as light yellow needles, m. p. and mixed m. p. 158—159° [from benzene–petroleum (3 : 1)].

Exhaustive elution of the alumina with the same solvent gave a further 0·32 g. of 9-benzoyloxyanthracene (total yield 15·2% based on anthracene). Further elution (iii) with 50% benzene–light petroleum gave a gum which when rubbed with ether gave 0·14 g. of a yellow solid. In boiling benzene this left a small white residue which, crystallised from xylene, had m. p. 286—288°, an ultra-violet absorption spectrum characteristic of a benzenoid compound, and an infra-red spectrum which did not show the presence of C–O or O–H groups; this material was perhaps an ether. The benzene filtrate from this trace of solid, on cooling, deposited yellow needles, m. p. 250—260°, which when warmed with alkaline sodium dithionite gave a deep red solution. After filtration this solution was aerated and the solid which separated was collected, dried, sublimed, and crystallised from benzene, it then proving to be anthraquinone, m. p. 275—276°.

The final fractions from exhaustion of the alumina column with solvents were uncrystallisable resins. This material (0·31 g.) was oxidised with hot chromium trioxide (0·4 g.) in acetic acid (10 c.c.) for 40 minutes and then poured into water. The solid again yielded anthraquinone (0·17 g.; m. p. and mixed m. p. 276—277°). On acidification the alkaline extracts yielded only 5 mg. of a brown resin.

Reaction of 1 : 2-*Benzanthracene.*—The hydrocarbon (5·4 g., 0·023 mole) with benzoyl peroxide (5·75 g., 0·023 mole) in chlorobenzene (100 c.c.) yielded carbon dioxide (0·307 g., 14·7%) and benzoic acid (2·51 g., 43·6%). Evaporation of the chlorobenzene left a red gum (8·4 g.) which was chromatographed in 2 : 3 benzene–light petroleum on neutral alumina. After recovery of 0·13 g. of unchanged hydrocarbon the main fractions consisted of red viscid oils (6 g.) which were re-united and then when rubbed with toluene gave a yellow solid (1·18 g.), m. p. 165—169° (crystallised from toluene). After passage through a fresh alumina column and a further crystallisation from toluene this proved to be 10-benzoyloxy-1 : 2-benzanthracene of m. p. 170·5—171° alone or mixed with an authentic specimen (Cook, *J.*, 1930, 1087) (Found: C, 85·7; H, 4·35. Calc. for $C_{25}H_{16}O_2$: C, 86·3; H, 4·6%). The crude benzoate (0·10 g.), when oxidised with chromic acid in acetic acid, gave benzoic acid (25 mg.), m. p. and mixed m. p. 121°, and a yellow semi-solid which on reduction with alkaline sodium dithionite gave a red solution indicative of the *meso*-quinone.

Reactions with 1 : 2-5 : 6-*Dibenzanthracene.*—(a) *Under nitrogen.* Heating the hydrocarbon (1·00 g.) and benzoyl peroxide (0·90 g.) in chlorobenzene (100 c.c.) at 80° for 36 hours under nitrogen afforded a light orange solution and carbon dioxide (0·127 g., 38·9%). Sodium hydrogen carbonate extraction gave benzoic acid (0·36 g., 40·1%). The solution, after concentration to 15 c.c. and storage at 0°, yielded 0·78 g. of unchanged hydrocarbon. The remainder after evaporation to dryness was passed in benzene (75 c.c.) through neutral alumina, whereby a further 0·11 g. of the hydrocarbon (total recovery, 89%) and 0·08 g. of a gum were obtained. On chromic acid oxidation this yielded less than 1 mg. of benzoic acid and a residue which did not exhibit the reactions of either of the possible dibenzanthraquinones.

(b) *In the presence of oxygen.* After 36 hours' reaction the product from 4·0 g. of hydrocarbon, 3·5 g. of benzoyl peroxide, and 170 c.c. of chlorobenzene was deep red. Extraction with sodium hydrogen carbonate yielded benzoic acid (1·67 g., 47·7%). After extraction with sodium hydroxide solution, then water, and drying, the solution was concentrated to 40 c.c. and stored at 0°. A light yellow solid (1·22 g.) was deposited, from which unchanged hydrocarbon (0·98 g.) was recovered. Evaporation of the remaining solution gave 4·1 g. of a resin which was passed in chloroform (10 c.c.) on to a column of neutral alumina, saturated with light petroleum (b. p. 60—80°). Elution with benzene–light petroleum (1 : 1) gave unchanged hydrocarbon (0·28 g.; total recovery, 31%). Elution with benzene then gave an orange solid (0·54 g.) which after successive crystallisation from benzene and chloroform–ethanol gave orange needles, m. p. 247—248·5°, their mixed m. p. with authentic 1 : 2-5 : 6-dibenzanthra-9 : 10-quinone being 247—249°. This substance gave a red solution when warmed with alkaline sodium dithionite and a violet colour with concentrated sulphuric acid. Further elution of the column with ether and then with chloroform gave a resin (1·52 g.) which could not be purified by further chromatography on alumina. The resin (1·25 g.) was oxidised for 6 hours with potassium dichromate (6 g.) in acetic acid (30 c.c.). Pouring into water, extraction with chloroform, and washing with aqueous sodium hydrogen carbonate gave, from the alkaline layer, 0·23 g. of benzoic acid, and from the chloroform layer 0·37 g. of a red solid which was extracted with hot benzene (25 c.c.). The dark red residue from this operation (0·04 g.) was sublimed at 295°/0·04 mm. and then crystallised from nitrobenzene; it then had m. p. 324—325° (decomp.) (Cook, *J.*, 1933, 1592, gives m. p. 326—327° for 1 : 2-5 : 6-dibenzanthra-3 : 4-quinone). Its identity was confirmed by formation of a yellow azine and by its bright blue colour in concentrated sulphuric acid. The filtrate from the above was passed down a column of activated alumina whereupon it separated into red and yellow bands. The yellow band gave a further 0·05 g. of the 9 : 10-quinone, m. p. and mixed m. p. 245—247°, whilst the red band gave a further 0·08 g. of the 3 : 4-quinone. In a second experiment 0·30 g. of the original resin after sublimation at 200°/0·04 mm. gave 6 mg. of benzoic acid, and at 300°/0·04 mm. a brown resinous solid which did not give quinone colour reactions with concentrated sulphuric acid.

(c) *Oxygen-absorption experiments.* For these the reaction flask was connected to a gas burette through a U-tube containing "Carbosorb." The system was evacuated at room temperature, dry oxygen was then admitted, and the flask was shaken vigorously in a thermostat at 80°, light being excluded and the system adjusted to atmospheric pressure after equilibrium had first been established. In experiment A (blank) 0·900 g. of benzoyl peroxide was used in 20 c.c. of chlorobenzene. In experiment B, 0·900 g. benzoyl peroxide (0·0037 mole) and 0·50 g. of dibenzanthracene (0·0018 mole) were used in 20 c.c. of chlorobenzene. Results were :

Time (hours)	1	3	17	48	72	96	Total (mole)
A (c.c. of O_2 taken up; N.T.P.) ...	0·9	1·1	2·2	4·4	6·4	6·4	$2{\cdot}85 \times 10^{-4}$
B ,, ,, ,,	4·4	6·5	9·9	10·2	10·2	10·2	$4{\cdot}55 \times 10^{-4}$

Both solutions became dark red within 5 hours.

Reaction with 3 : 4-*Benzopyrene.*—The hydrocarbon (4·0 g., 0·0158 mole) with benzoyl peroxide (3·84 g., 0·0158 mole) in chlorobenzene (170 c.c.) yielded benzoic acid (1·80 g., 46·9%) but only 0·037 g. (2·6%) of carbon dioxide. The solution was concentrated to 15 c.c., and stored at 0° for 24 hours, 3·03 g. of a solid, m. p. 190—215°, separating from the black liquid. Crystallisation from benzene (30 c.c.) gave a light yellow solid, m. p. 218—219° (1·98 g., 33·6% based on the hydrocarbon). Two further crystallisations from benzene raised the m. p. to 220—221° (Found: C, 87·5; H, 4·5. $C_{27}H_{16}O_2$ requires C, 87·2; H, 4·35%) and admixture with authentic 5-*benzoyloxy*-3 : 4-*benzopyrene,* synthesised as described below, did not depress the m. p. 5-Hydroxy-3 : 4-benzopyrene was prepared by hydrolysis of the reaction product of the corresponding 5-acetoxy-compound and *n*-butylmagnesium bromide, as described by Fieser and Hershberg (*J. Amer. Chem. Soc.*, 1939, **61**, 1565). This phenol (0·15 g.), together with benzoic anhydride (0·3 g.), was dissolved in pyridine (5 c.c.), and the whole was warmed on a water-bath at 100° for an hour and then poured into an excess of dilute hydrochloric acid. After extraction with warm benzene the organic layer was shaken with sodium hydrogen carbonate solution, then water, and dried ($CaCl_2$). On concentration of the solution to 3 c.c. and cooling, a yellow solid (0·15 g.), m. p. 218—219°, was deposited; after crystallisation from benzene this had m. p. 220·5—221·5° and was identical with the previously described benzoate (Found : C, 86·8; H, 4·3%).

Reaction with Phenanthrene.—Phenanthrene (10 g.) with benzoyl peroxide (13·6 g.) in chlorobenzene (250 c.c.) gave carbon dioxide (2·42 g., 48·9%) and benzoic acid (3·80 g., 28%). 85% of the hydrocarbon was recovered unchanged and no phenanthrene derivatives could be isolated by chromatography of the residual solutions : chlorodiphenyls and phenyl benzoate were present.

Reaction with Chrysene.—When carried out exactly as above, this gave a 57·7% yield of carbon dioxide, and 87% of the hydrocarbon was recovered unchanged.

Reaction with 9-*Methylanthracene.*—Only 2·31% of carbon dioxide was evolved from the reaction of 9-methylanthracene (10 g., 0·052 mole.) with benzoyl peroxide (12·6 g., 0·052 mole.) in chlorobenzene (150 c.c.); a second experiment gave 2·01% of carbon dioxide. On cooling, 0·08 g. of a yellow product (VI; R = H), m. p. 306—311° (decomp.), was deposited. Extraction of the chlorobenzene solution with aqueous sodium hydrogen carbonate gave benzoic acid (6·56 g., 52·0%; a second experiment gave 51·3%). After drying ($CaCl_2$), the chlorobenzene solution was concentrated to 30 c.c. and kept at 0°, 1·15 g. of a yellow solid (D1) being obtained. The chlorobenzene was then evaporated and the resulting gum was dissolved in benzene (30 c.c.). Storage overnight yielded a white solid (D2) (0·08 g.). When, in a second experiment, the benzene solution was chromatographed immediately, D2 was eluted as the first fraction.

After purification, the compound (VI; R = H) crystallised from toluene in long fine needles, m. p. 308—313° (decomp.) (Found: C, 94·2; H, 6·0. Calc. for $C_{30}H_{22}$: C, 94·2; H, 5·8%). Its solution in chloroform was strongly fluorescent in ultra-violet light. Its absorption spectra in both the infra-red and the ultra-violet region were identical with those of 1 : 2-di-9′-anthranylethane and admixture with this compound did not depress the m. p.

Solid D 1 crystallised from toluene as a mixture of needles and prisms. This was heated with a small volume of toluene and filtered. The nearly white residue was dissolved in an excess of boiling toluene and allowed to cool slowly, a mixture of large opaque hexagonal prisms (elongated along one radial axis) and small transparent rhombohedral prisms then being deposited (Found: C, 94·2; H, 5·75. $C_{30}H_{22}$ requires C, 94·2; H, 5·8%). These two crystalline forms were separated by hand; both softened and became yellow on a m. p. block at 270—280° and finally melted at 308—313° (decomp.). A chloroform solution of the mixture was not fluorescent and exhibited an ultra-violet spectrum characteristic of a benzenoid substance (Fig. 2, *D*).

The *compound* D 2, after two recrystallisations from toluene, gave deep rhombic prisms which melted almost completely at 230—236°, then resolidified as the temperature was raised, and finally melted with decomposition at 278—284°. Recrystallisation from glacial acetic acid did not alter this behaviour (Found: C, 93·9; H, 5·9. $C_{30}H_{22}$ requires C, 94·2; H, 5·8%). The infra-red and ultra-violet spectra were almost identical with those of hydrocarbon D1.

The benzene mother-liquors from the separation of D 2 were diluted with light petroleum (b. p. 60—80°) and chromatographed on neutral alumina. (i) Evaporation of the mixed solvent gave substance D 2 (10 mg.). (ii) Elution with 50% benzene–light petroleum gave a light yellow gum which on treatment with acetone–ethanol deposited a solid (0·08 g.), m. p. 229—236°. (iii) Continued elution with the same mixed solvent gave more yellow gum (0·26 g.) which when covered for some days with ethyl acetate–ethanol and then crystallised from toluene yielded a solid (25 mg.), m. p. 226—230°.

The mother-liquors from this substance were again chromatographed on neutral alumina, and the middle fractions which were then extracted with benzene–light petroleum and had m. p. range 175—180° were bulked and crystallised twice from toluene–acetic acid, giving light yellow needles, m. p. 180—181° (Found: C, 85·2; H, 5·3%; *M*, 268. $C_{22}H_{16}O_2$ requires C, 84·7; H, 5·2%; *M*, 312). The m. p. of this product was not depressed by admixture with authentic 9-*benzoyloxy*-10-*methylanthracene* (see below) and both samples had the same infra-red spectrum.

The later fractions from elution of the original reaction mixture were oily solids which, after being rubbed with ether, solidified and had m. p. 238—241°. The final band eluted with ethyl acetate, was a gum which on treatment with acetone–ethanol yielded a yellow solid (0·35 g.), m. p. 227—237°. This was bulked with previous solids having the same m. p. range (see above), dissolved in 3 : 2 benzene–light petroleum and again chromatographed on neutral alumina. The solids obtained by rubbing the middle fractions of these eluates with ether were crystallised twice from toluene, giving yellow needles, m. p. 244—245° (Found: C, 88·2; H, 5·2%; *M*, 425. $C_{37}H_{26}O_2$ requires C, 88·4; H, 5·2%; *M*, 503). This corresponds to 1-9′-*anthranyl*-2-(10-*benzoyloxy*-9-*anthranyl*)*ethane* (VI; R = Ph·CO$_2$) and the infra-red spectrum (Fig. 3, *F*) further supports its identity.

Eventually the residue from the original chromatogram was extracted with chloroform, and gave an orange solid (0·15 g.). Further chromatography of this, with elution by benzene, gave anthraquinone (55 mg., m. p. and mixed m. p. 278—279°; red colour in warm alkaline sodium dithionite). Alkaline hydrolysis of the resins which accompanied this material yielded benzoic acid (0·3 g.) and a further 0·19 g. of anthraquinone. No 9-hydroxymethylanthracene could be found in any fraction of eluted material.

Depolymerisation of D 2.—35 Mg. of the hydrocarbon were heated in ethyl benzoate (2 c.c.) for ½ hour at 180°. The resulting yellow solution was concentrated, the white unchanged hydrocarbon was separated, and the mother-liquors were then reduced to dryness under reduced pressure. The ultra-violet spectrum of the resulting solid (Fig. 2, *B*) was almost identical with that of 1 : 2-di-9′-anthranylethane (Fig. 2, *A*). On account of this depolymerisation, attempts at determination of the molecular weights of both D 1 and D 2 by Rast's method in camphor gave values approximating to that of the monomer (VI; R = H).

Photo-polymerisation of 1 : 2-*Di*-9′-*anthranylethane*.—50 Mg. of (VI; R = H) in pure benzene (50 c.c.) were irradiated under a reflux condenser for 24 hours with a 250-w Hanovia ultra-violet lamp. The hot solution was then filtered and, after cooling, colourless prisms (5 mg.) were collected. Their solution in chloroform was not fluorescent and the ultra-violet spectrum revealed destruction of the anthracene-like absorption of the starting material. The m. p. and crystalline form of the product were the same as those of the hexagonal prisms of hydrocarbon D 1.

Reference Materials.—(a) *9-Benzoyloxy-*10*-methylanthracene.* 10-Methylanthrone (1·2 g.; Barnett and Matthews, *Ber.*, 1926, **59**, 768) was warmed on a water-bath for an hour with pyridine (6 c.c.) and benzoic anhydride (2·5 g.) and the whole then poured into water. The oil which separated was dissolved in ether, washed with dilute hydrochloric acid, sodium hydrogen carbonate, and water and then dried ($CaCl_2$). The solid obtained by evaporation of the ether was crystallised twice from toluene, and gave fine needles, m. p. 180—181° (Found: C, 84·7; H, 5·2%).

(b) 1 : 2*-Di-9′-anthranylethane.* This was prepared by reduction of 10-methyleneanthrone with zinc and hydrochloric acid in acetic acid solution (Barnett and Matthews, *loc. cit.*) (Found: C, 94·0; H, 6·0. Calc. for $C_{30}H_{22}$: C, 94·2; H, 5·8%). Its m. p. and infra-red spectrum in both α-bromonaphthalene and paraffin paste (Fig. 3, *C*) were identical with those previously recorded for compound (VI; R = H).

(c) 10 : 10′*-Dimethyl-*9 : 9′*-dianthranyl.* This was prepared by reduction of 10-methylanthrone with zinc dust and ammonia (Barnett and Matthews, *loc. cit.*), and its infra-red spectrum was determined both in α-bromonaphthalene and in paraffin paste (Fig. 3, *B*). Our analysis accords with the formula stated above (Found: C, 94·2; H, 5·75. Calc. for $C_{30}H_{22}$: C, 94·2; H, 5·8%). For comparison, the infra-red spectra of 9-methylanthracene and of 9 : 10-dihydro-9-methylanthracene (Sieglitz and Marx, *Ber.*, 1923, **56**, 1619) were also measured (Fig. 3, *A* and *D*).

The use of α-bromonaphthalene as a pasting medium for the elucidation of infra-red spectra in the aliphatic C—H stretching region (*ca.* 3·4 μ) was suggested to us by Dr. F. B. Strauss. On account of its availability and aromatic character it is superior to perfluorinated paraffins for the detection of alkyl side-chains in aromatic systems.

Microanalyses and measurements of both ultra-violet and infra-red spectra were carried out by Drs. Strauss and Weiler. This investigation has been carried out on behalf of the British Empire Cancer Campaign, the Council of which we thank for a grant made to one of us (I. M. R.) and for a gift of 3 : 4-benzopyrene. We also thank Professor A. Haddow, M.D., for his interest in the work.

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[*Received, February* 20*th*, 1952.]