493. *Thiyl Radicals. Part IV.*[1] *Reactions, Catalysed by Ferrous Ion, of Polycyclic Aromatic Hydrocarbons with t-Butyl Hydroperoxide and Mercapto-compounds.*

By A. L. J. Beckwith and (Miss) Low * Beng See.

Buta-1,3-diene, thioacetic acid, and t-butyl hydroperoxide interact readily in the presence of catalytic amounts of ferrous ion, formed *in situ* from ferrocene. The free-radical nature of the reaction has been demonstrated by the isolation of an additive dimer of buta-1,3-diene containing two acetylthio-groups. Anthracene reacts with free acetylthio-radicals, similarly generated, yielding 9-(acetylthio)anthracene and 9,10-di(acetylthio)-9,10-dihydroanthracene. Analogous products were obtained when anthracene was treated with free thiyl radicals derived from thiobenzoic acid, mercaptoacetic acid, butane-1-thiol, *N*-acetyl-L-cysteine, and thiophenol.

1,2-Benzanthracene, 1,2-benzopyrene, pyrene, and perylene undergo attack by acetylthio-radicals at the positions of maximum free valence. When treated with free carboxymethylthio-radicals, 1,2-benzopyrene affords 3,6-di(carboxymethylthio)-1,2-benzopyrene. Phenanthrene and 1,2:5,6-dibenzanthracene do not react with free thiyl radicals.

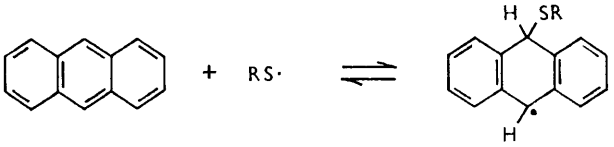
Reactions of anthracene with thiophenol and oxygen, and with benzoylthio-radicals generated photolytically from dibenzoyl disulphide, are described.

The hypothesis [2] that the reaction of mercapto-compounds and oxygen with anthracene and other polycyclic aromatic hydrocarbons [1-4] proceeds by a free-radical mechanism involving consecutive additions of a free thiyl radical and molecular oxygen to the aromatic nucleus is supported by considerable experimental evidence,[1-3] and has sound analogy in the reactions of olefins with thiols and oxygen.[5] On the other hand, the addition of thiyl radicals to aromatic systems appears to be without precedent; indeed, an attempt to effect substitution of 1,2-benzopyrene with carboxymethylthio-radicals formed photolytically from mercaptoacetic acid was unsuccessful, the sole product being 1,2-benzopyren-3-ylacetic acid.[6] Only the starting material was isolated when 1,2-benzopyrene was treated with ethyl mercaptoacetate and Fenton's reagent.[6] Also, no products containing thio-substituents have been obtained from dehydrogenation of hydroaromatic compounds

* Author's surname.

[1] Part III, Beckwith and Low, *Austral. J. Chem.*, 1964, **17**, 109.
[2] Beckwith and Low, *J.*, 1961, 1304.
[3] Beckwith and Low, *Austral. J. Chem.*, 1963, **16**, 845.
[4] Mikhailov and Blokhina, *Doklady Akad. Nauk S.S.S.R.*, 1951, **80**, 373; *Probl. Mekhanizma Org. Reakt. Akad. Nauk, Ukr. S.S.R.*; *Otdel Fiz-Mat. i Khim. Nauk*, 1953, 215.
[5] Kharasch, Nudenberg, and Mantell, *J. Org. Chem.*, 1951, **16**, 524; Oswald, *ibid.*, 1961, **26**, 842; Oswald, Noel, and Fisk, *ibid.*, 1961, **26**, 3974; Ford, Pitkethly, and Young, *Tetrahedron*, 1958, **4**, 325; Bredereck, Wagner, and Kottenhahn, *Chem. Ber.*, 1960, **93**, 2415.
[6] Conway and Tarbell, *J. Amer. Chem. Soc.*, 1956, **78**, 2228.

with disulphides [7] or with αα′-azoisobutyronitrile catalysed by thiols,[8] although both reactions are considered to involve the intermediate formation of free thiyl radicals. To resolve this apparent contradiction, it was postulated [2] that the addition of a thiyl radical to an aromatic nucleus (*e.g.*, anthracene), like that to an olefinic bond,[9] is a reversible



(I) (I)

process. We suggest that, under the conditions employed for dehydrogenation, the equilibrium so favours the dissociation of the adduct (I) that the rate of formation of stable products by this route is negligible. It is a necessary corollary of this hypothesis that the formation of thio-derivatives from aromatic hydrocarbons and thiyl radicals, generated by a variety of methods, should proceed efficiently under the mild conditions employed in our earlier studies.[1-3] We now describe experiments designed to test the validity of this assumption.

The photolysis of disulphides [10] provides a convenient low-temperature procedure for the generation of thiyl radicals. Accordingly, a solution of anthracene and dibenzoyl disulphide in benzene was illuminated in a quartz vessel with sunlight. The major product was the photo-dimer of anthracene, but 9-(benzoylthio)anthracene (IV; R = Bz) was also isolated in low yield. Although this result appears to support the contention that substitution of aromatic hydrocarbons may be effected by thiyl radicals at ambient temperature, the possibility that the reaction involves an excited state of anthracene cannot entirely be discounted. Also, later experiments [11] indicated that photolysis of dibenzoyl disulphide proceeds partly by C–S bond fission, with the production of benzoyl radicals. Therefore, another method for non-pyrolytic generation of thiyl radicals was sought.

The low S–H bond strength in thiols [12] should render them particularly susceptible to hydrogen-atom abstraction by suitable oxy-radicals; indeed, the production of free thiyl radicals in aqueous solution by oxidation of mercapto-compounds with hydroxyl radicals generated by Fenton's method has been reported.[13] This reaction was adapted for use in non-polar solvents by using t-butyl hydroperoxide as a source of alkoxy-radicals. We considered that ferrous-ion-catalysed oxidation of a thiol by t-butyl hydroperoxide would proceed as follows:

$$Fe^{2+} + Bu^tO{\cdot}OH \longrightarrow Bu^tO{\cdot} + Fe^{3+} + OH^- \quad (2)$$

$$Bu^tO{\cdot} + R{\cdot}SH \longrightarrow Bu^tOH + RS{\cdot} \quad (3)$$

$$2RS{\cdot} \longrightarrow RS{\cdot}SR \quad (4)$$

$$2Fe^{3+} + 2R{\cdot}SH \longrightarrow 2Fe^{2+} + RS{\cdot}SR \quad (5)$$

Preliminary experiments revealed that mercapto-compounds were, in fact, rapidly converted into the appropriate disulphides when treated in benzene with t-butyl hydroperoxide and an iron salt (or, more conveniently, ferrocene, which is readily oxidised to ferric ion by peroxides [14]). The occurrence of free thiyl radicals as intermediates in these

[7] Ritter and Sharpe, *J. Amer. Chem. Soc.*, 1937, **59**, 2351; Nakasaki, *J. Chem. Soc. Japan*, 1953, **74**, 403, 518.
[8] Bickel and Kooyman, *Nature*, 1952, **170**, 211; Beckwith and Waters, *J.*, 1957, 1001.
[9] Walling and Helmreich, *J. Amer. Chem. Soc.*, 1959, **81**, 1144; Neureiter and Bordwell, *ibid.*, 1960, **82**, 5354.
[10] Cole, *Nature*, 1963, **198**, 1083; Eager and Savige, *Photochem. and Photobiol.*, 1963, **2**, 25; Walling and Rabinowitz, *J. Amer. Chem. Soc.*, 1959, **81**, 1137; Cohen and Wang, *ibid.*, 1955, **77**, 4435.
[11] Acott and Beckwith, unpublished work.
[12] Franklin and Lumpkin, *J. Amer. Chem. Soc.*, 1952, **74**, 1023.
[13] Jenner and Lindsey, *J. Amer. Chem. Soc.*, 1961, **83**, 1911.
[14] Beckwith and Leydon, *Tetrahedron Letters*, 1963, 385.

reactions was confirmed by conducting the oxidation of thioacetic acid in the presence of an excess of buta-1,3-diene. As Jenner and Lindsey [13] pointed out, monomeric addition products of butadiene with a thiol may arise either by free-radical or polar processes, but the formation of an additive dimer (III, and appropriate isomers) is indicative of the intermediate formation of the allylic radical (II) and hence diagnostic of a free-radical mechanism. The crude product, when fractionated, afforded a liquid having physical constants, elemental analysis, molecular weight, and infrared spectrum in accord with its formulation as a mixture of the additive dimer (III; R = Ac) and appropriate isomers.

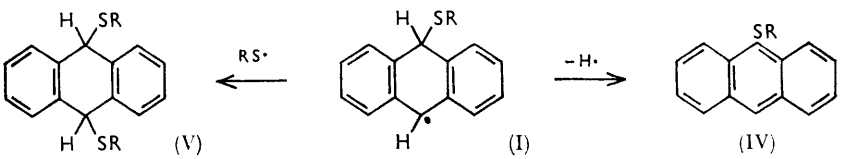
$$RS\cdot + CH_2{:}CH{\cdot}CH{:}CH_2 \longrightarrow \underset{(II)}{[RS{\cdot}CH_2{\cdot}CH{=}{=}CH{=}{=}CH_2]\cdot} \longrightarrow \underset{(III)}{RS{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH_2{\cdot}SR}$$

Thus, the formation of free acetylthio-radicals by ferrous-ion-catalysed oxidation of thioacetic acid was confirmed.

The reactions of anthracene with thiyl radicals generated oxidatively from a variety of mercapto-compounds were next investigated. When anthracene, t-butyl hydroperoxide, ferrocene, and thioacetic acid were mixed in benzene, there was initially no visible indication of reaction. Evidently, conversion of ferrocene into ferrous ion had not occurred, since a rapid reaction ensued on adding a solution obtained by oxidising a small amount of ferrocene with t-butyl hydroperoxide in hot benzene. The products, isolated chromatographically, were 9-(acetylthio)anthracene (IV; R = Ac) and two isomers of 9,10-di(acetylthio)-9,10-dihydroanthracene (V; R = Ac). Di-9-anthryl disulphide, which was also obtained, is considered to be an artefact arising from 9-(acetylthio)anthracene by hydrolysis and oxidation during chromatography.

Anthracene, when treated with thiobenzoic acid, t-butyl hydroperoxide, and ferrocene, afforded two isomers of 9,10-di(benzoylthio)-9,10-dihydroanthracene (V; R = Bz), and 9-(benzoylthio)anthracene (IV; R = Bz), but the analogous reaction with mercaptoacetic acid gave only one isomer of the dihydro-compound (V; R = $CH_2{\cdot}CO_2H$) together with 9-(anthrylthio)acetic acid (IV; R = $CH_2{\cdot}CO_2H$).

The formation of these products is consistent with a mechanism involving intermediate formation of the adduct (I) as in reaction (1). Hydrogen-atom abstraction from the intermediate (I) by a thiyl or t-butoxy-radical yields the fully aromatic product (IV),



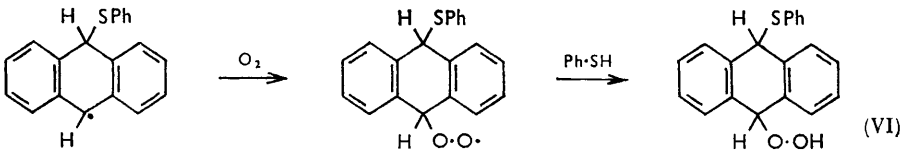
and formation of the dihydro-anthracene (V) proceeds by addition of a second thiyl radical. The isolation of these products in good yield provides a measure of the facility with which addition of thiyl radicals to anthracene occurs, for the steps in the suggested mechanism compete directly for thiyl radicals with the rapid dimerisation reaction (4).

Similar results were obtained when anthracene was treated with mercapto-compounds and oxygen,[2] although the yields of products were less. However, a parallel between the two types of reaction was not invariably observed. For example, the reaction of anthracene with butane-1-thiol and oxygen yielded no identifiable pure product [the presence of 9-(n-butylthio)anthracene was indicated by chromatography],[1] whereas addition of t-butyl hydroperoxide and ferrocene to anthracene and butane-1-thiol afforded 9,10-di-(n-butylthio)-anthracene in moderate yield. Its formation may be ascribed either to hydrogen-atom abstraction from the dihydro-compound (V; R = Bu^n), or to the further attack of n-butylthio-radicals on 9-(n-butylthio)anthracene (IV; R = Bu^n). It may be relevant that separate experiments have shown n-butylthio-radicals to be more efficient as hydrogen-atom acceptors than radicals derived from other types of mercapto-compound.[11]

The reaction of anthracene with *N*-acetyl-L-cysteine, t-butyl hydroperoxide, and ferrocene proceeded smoothly in tetrahydrofuran, and afforded *N*-acetyl-*S*-(9-anthryl)-L-cysteine (IV; R = CH_2·CHNAc·CO_2H). We alluded previously to possible biochemical implications of this type of reaction.[1,2]

In view of the facility with which anthracene underwent the transformations described above, its recovery in high yield after treatment in the usual way with thiophenol was surprising. Much the same result was observed when ferric chloride was employed as catalyst, although in this case 9-(phenylthio)anthracene was isolated in very small yield and 9,10-dihydro-9,10-di(phenylthio)anthracene was detected chromatographically. Because of the discordance between these results and those obtained when anthracene was shaken with thiophenol under oxygen,[2] the latter reaction was reinvestigated. As before, an unstable compound formulated as 9,10-dihydro-9-hydroperoxy-10-(phenylthio)anthracene (VI) was obtained in moderate yield. An improved isolation technique also allowed the separation of an unidentified compound, $C_{26}H_{20}S$, and 9,10-dihydro-9,10-di(phenylthio)anthracene, neither of which had been obtained previously.[2] The latter compound was identified from its elemental analysis, physical properties, and ready conversion into 9-(phenylthio)anthracene on treatment with mineral acid.

The differences between the two types of reaction involving thiophenol may be rationalised by consideration of the reaction mechanisms. Both transformations must proceed by way of the adduct (I; R = Ph) formed in the equilibrium step (1). We suggested [2] that the formation of the hydroperoxide (VI) involves the following mechanism:



(VI)

The efficiency of this process, as compared with the reaction involving t-butyl hydroperoxide, is attributable to the high strength of the C–O bond relative to the C–S bond.[15] Also, the high concentration of oxygen in the mixture undoubtedly facilitates the formation of the hydroperoxide (VI).

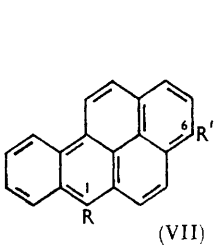
The relatively low yields in the reaction of anthracene and t-butyl hydroperoxide with thiophenol may be attributed to resonance stabilisation of the phenylthio-radical, which retards its reaction with the adduct (I; R = Ph) and which causes the position of equilibrium in step (1) to be less favourable. Also, it is conceivable that the dimerisation (4), which competes with the formation of anthracene derivatives, is especially favoured in the case of phenylthio-radicals where the strength of the S–S bond in the resultant disulphide may be enhanced by conjugation involving expansion of the sulphur outer shell.[16]

The reactions of thiyl radicals with phenanthrene, pyrene, 1,2-benzanthracene, 1,2:5,6-dibenzanthracene, perylene, and 1,2-benzopyrene were studied. Of these, only phenanthrene and the dibenzanthracene failed to react with free radicals derived from mercaptoacetic acid by ferrous-ion-catalysed oxidation with t-butyl hydroperoxide, but the products from the others resisted purification except that from 1,2-benzopyrene, which afforded 3,6-di(carboxymethylthio)-1,2-benzopyrene (VII; R = R′ = S·CH_2·CO_2H), isolated as its dimethyl ester. The structure of this ester was determined by oxidation to 1,2-benzopyrene-3,6-dione, identified by its ultraviolet spectrum and by thin-layer chromatography. The formation of the di-acid may involve either hydrogen-atom abstraction from the appropriate dihydro-compound, or two consecutive substitutions, at the 3- and the 6-position.

The isolation of pure products derived from polycyclic hydrocarbons was more readily

[15] Lovering and Laidler, *Canad. J. Chem.*, 1960, **38**, 2367.
[16] Foss and Tjomsland, *Acta Chem. Scand.*, 1958, **12**, 44, 1799; Bergson, *Arkiv Kemi*, 1958, **13**, 11; Krebs, *Z. Naturforsch.*, 1957, **12**b, 795.

accomplished when thioacetic acid was the source of thiyl radicals. Nevertheless, no evidence of reaction between acetylthio-radicals and phenanthrene or 1,2:5,6-dibenzanthracene was obtained. In the case of phenanthrene, the failure to undergo substitution



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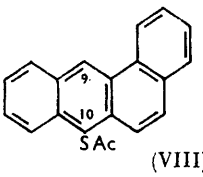

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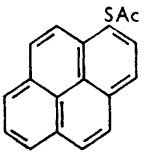

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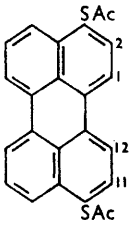

(X)

gives evidence of the relatively low intrinsic reactivity of the system, in accord with theoretical predictions.[17] 1,2:5,6-Dibenzanthracene, however, has much higher theoretical indices of reactivity,[17] and its failure to react must be attributed to steric hindrance on the *meso*-positions by the protons at the 6′ and 6″-positions. Its unexpectedly low reactivity towards attack by a variety of reagents had been noted by other workers.[18]

In some cases reaction of the hydrocarbons with thioacetic acid, t-butyl hydroperoxide, and ferrocene afforded the same products (albeit in higher yield) as were obtained from analogous reactions using oxygen as the oxidising agent.[1] For example, 1,2-benzanthracene was converted in excellent yield into a mixture of 10-acetylthio-1,2-benzanthracene (VIII) and 9,10-di(acetylthio)-9,10-dihydro-1,2-benzanthracene, and 3-acetylthio-1,2-benzopyrene (VII; R = SAc, R′ = H) was obtained from 1,2-benzopyrene.

The superiority of the method using t-butyl hydroperoxide and ferrocene for the introduction of thio-substituents was demonstrated in experiments with pyrene and perylene, each of which failed to react with free thiyl radicals generated by aerial oxidation of thioacetic acid.[1] However, when treated with thioacetic acid, t-butyl hydroperoxide, and ferrocene, these compounds were converted into 1-(acetylthio)pyrene (IX) and 3,10-di-(acetylthio)perylene (X), respectively. The former was identical with an authentic specimen, and the latter was identified by its oxidation to perylene-3,10-dione.

In the absence of evidence to the contrary we assume that the reactions of higher polycyclic aromatic hydrocarbons proceed by mechanisms similar to that suggested for anthracene. It is noteworthy that, in each case, attack occurs at the position or positions of highest free valance.[17,19] Further experiments designed to test this hypothesis are in hand.

In most cases, compounds needed for comparison were available from earlier studies.[1-3] However, 9-(phenylthio)anthracene was conveniently prepared by the reaction of 9-anthryl-lithium with diphenyl disulphide, and 1-(acetylthio)pyrene (IX) resulted from reductive acetylation of di-1-pyrenyl disulphide, prepared from pyrene by way of 1-pyrenyl thiocyanate.[20]

Experimental

Unless otherwise stated, all reactions and working-up procedures were conducted under nitrogen. Thin-layer chromatography was carried out on alumina G using toluene–tetrahydrofuran (20 : 1) as eluant.

Photolysis of Dibenzoyl Disulphide in the Presence of Anthracene.—Dibenzoyl disulphide (2·74 g.) was added to anthracene (0·89 g.) in oxygen-free benzene (100 ml.), and the mixture was illuminated through quartz with sunlight for 10 hr., during which time the disulphide

[17] Coulson and Daudel, "Dictionary of Values of Molecular Constants," 1955, Vol. II.
[18] Ariyan and Wiles, *J.*, 1962, 1725; Wood and Fieser, *J. Amer. Chem. Soc.*, 1940, **62**, 2674; 1941, **63**, 2323; Fieser and Hershberg, *ibid.*, 1938, **60**, 1893, 2542; Fieser and Campbell, *ibid.*, 1938, **60**, 1142.
[19] Hall, *Trans. Faraday Soc.*, 1957, **53**, 573.
[20] Lund and Berg, *Kgl. danske Videnskab. Selskab, Mat.-fys. Medd.*, 1946, **22**, No. 15, 1.

dissolved, the solution turned brown, and the photo-dimer of anthracene was slowly precipitated. The mixture was filtered and the filtrate was evaporated under reduced pressure. Crystallisation of the residue from benzene afforded dibenzoyl disulphide (1·65 g.) and anthracene (25 mg.). The residue, obtained by evaporation of the mother-liquor, was separated chromatographically on alumina into sulphur (5 mg.), anthracene (0·11 g.), anthraquinone (20 mg.), and 9-(benzothio)anthracene (0·1 g.), yellow prisms, m. p. and mixed m. p. 222—224° (from benzene–hexane).

Reaction of Buta-1,3-diene with Thioacetic Acid.—Buta-1,3-diene was bubbled rapidly into a stirred solution of ferrocene (0·1 g.) in benzene (200 ml.). After 30 min., simultaneous dropwise addition, at equal rates, of solutions of thioacetic acid (20 ml.) in benzene (30 ml.) and t-butyl hydroperoxide (13 g.) in benzene (34 ml.) was commenced. The mixture became warm. After the addition (1 hr.) the introduction of butadiene was continued for 45 min., by which time the mixture gave a negative test for peroxide. The solvent was then evaporated and the residue fractionally distilled under reduced pressure giving: (i) crude diacetyl disulphide (9·5 g.), b. p. 30—33°/0·6 mm.; (ii) a colourless liquid (4 g.), b. p. 76—78°/0·7 mm. (Found: C, 40·2; H, 5·3; S, 35·8%); (iii) a yellow liquid (2·1 g.), b. p. 129—140°/0·7 mm. (Found: C, 53·5; H, 7·0; S, 25·8%); and (iv) di(thioacetoxy)octadiene (2·5 g.), b. p. 148—153°/0·3 mm. [Found: C, 56·5; H, 7·1; S, 24·0%; *M* (Rast), 224. Calc. for $C_{12}H_{18}O_2S_2$: C, 55·8; H, 7·0; S, 24·8%; *M*, 258], $\nu_{max.}$ (film) 1690 (S·CO·CH_3), 1640 (C:C), 965 (*trans* CH:CH), 995 and 920 cm.$^{-1}$ (CH:CH_2).

Reactions of Mercapto-compounds with Anthracene.—General method. Ferrocene (50 mg.) and t-butyl hydroperoxide (3 g., 0·032 mole) in benzene (5 ml.) were added dropwise with stirring to a suspension of anthracene (2 g., 0·011 mole) in benzene (30 ml.) containing an excess of the mercapto-compound (0·05—0·13 mole). Heat was evolved and transient colours (*e.g.*, red, purple) were observed. The mixture was set aside until the colour reverted to pale yellow, and then filtered from unchanged anthracene. The filtrate was evaporated under reduced pressure, and the residue fractionally crystallised and chromatographed on alumina. The products were identified, unless otherwise specified, by mixed m. p. and ultraviolet and infrared spectra.[2,3]

Thioacetic acid. The reaction time was 2 hr. Products included: an isomer (0·18 g.), m. p. 145—147°, of 9,10-di(acetylthio)-9,10-dihydroanthracene, a second isomer (0·10 g.), m. p. 124—126°, 9-(acetylthio)anthracene (0·74 g.), and di-(9-anthryl) disulphide (0·3 g.). Anthracene (0·16 g.) was recovered.

Thiobenzoic acid. The mixture was worked up after 3 days, and afforded: anthracene (0·26 g.), an isomer (0·25 g.), m. p. 193—194°, of 9,10-di(benzoylthio)-9,10-dihydroanthracene, a second isomer (0·22 g.), m. p. 201—203°, and 9-(benzoylthio)anthracene (50 mg.).

Mercaptoacetic acid. The reaction was complete after 15 min. Filtration afforded 9,10-di-(carboxymethylthio)-9,10-dihydroanthracene (3·1 g.). (9-Anthrylthio)acetic acid (0·12 g.) was obtained from the filtrate.

Butane-1-thiol. The reaction, which was very slow, was allowed to proceed for 3 days. The mixture was worked up in the usual way, giving anthracene (0·54 g.), anthraquinone (80 mg.), and a yellow oil, which was chromatographed thrice, using light petroleum (b. p. 32—34°) and hexane as eluants, to give 9,10-*di-(n-butylthio)anthracene* (0·14 g.) as fluorescent, green-yellow needles, m. p. 61—62° (Found: C, 74·6; H, 7·4; S, 17·7. $C_{22}H_{26}S_2$ requires C, 74·5; H, 7·4; S, 18·1%), $\lambda_{max.}$ 222, 244 (infl.), 253 (infl.), 264, 352 (infl.) 370, 387, and 409 mμ (ε 10,845, 21,000, 37,800, 77,400, 2317, 4980, 7537, and 8070).

N-*Acetyl*-L-*cysteine*.[21] The reaction was conducted on one quarter of the above scale in tetrahydrofuran (20 ml.). After standing overnight at room temperature the mixture was warmed for 30 min. Filtration of the cooled mixture gave anthracene (0·23 g.). The filtrate was diluted with benzene, washed with water, and extracted with aqueous sodium carbonate. Acidification of the extract afforded *N*-acetyl-*S*-(9-anthryl)cysteine (55 mg.). Evaporation of the benzene layer gave anthracene (0·24 g.).

Thiophenol. Ferric chloride was used as a catalyst in place of ferrocene, and acetic acid (1·5 ml.) was added to the mixture. The reaction time was 5 hr. Anthracene (1·8 g.) and 9-(phenylthio)anthracene (0·12 g.) were isolated in the usual way. 9,10-Dihydro-9,10-di-(phenylthio)anthracene was detected by thin-layer chromatography but could not be obtained pure. 90% of the thiol was converted into diphenyl disulphide.

[21] Smith and Gorin, *J. Org. Chem.*, 1961, **26**, 820; Pirie and Hele, *Biochem. J.*, 1933, **27**, 1716.

Reaction of Anthracene with Thiophenol and Oxygen.—A mixture of anthracene (1·8 g.), thiophenol (10 ml.), and benzene (25 ml.) was shaken under oxygen for 4·5 hr., during which time 219 ml. of gas were absorbed. Filtration afforded a crystalline compound, tentatively formulated as 9,10-dihydro-9-(phenylthio)anthracene 10-hydroperoxide, which decomposed, sometimes with violence, when heated or left in the air, and which liberated iodine from acidified potassium iodide solution. The filtrate was evaporated, and the residue separated by fractional crystallisation and chromatography into diphenyl disulphide, anthracene, anthraquinone (30 mg.), an unidentified substance (30 mg.), m. p. 244—245·5° (Found: C, 85·5; H, 5·4. Calc. for $C_{26}H_{20}S$: C, 85·7; H, 5·5%), and 9,10-*dihydro*-9,10-*di*(*phenylthio*)*anthracene* (0·45 g.) needles, m. p. 117—127° (from hexane) (Found: C, 79·3; H, 5·3; S, 16·0. $C_{26}H_{20}S_2$ requires C, 78·8; H, 5·1; S, 16·1%). When warmed with acetic acid containing 1% of sulphuric acid, the dihydro-compound was quantitatively converted into 9-(phenylthio)anthracene.

Reaction of 1,2-*Benzopyrene with Mercaptoacetic Acid.*—t-Butyl hydroperoxide (0·7 g.) and ferrocene (8 mg.) in benzene (2 ml.) were added to 1,2-benzopyrene (0·39 g.) and mercaptoacetic acid (1 ml.) in benzene (10 ml.), and the mixture was set aside overnight. A solid (0·43 g.), m. p. 160—200°, was collected by filtration and washed with hot benzene (5 ml.). The insoluble material (0·34 g.) was treated with diazomethane in ether, and the resultant crude ester was chromatographed on alumina (neutral, activity 2). The only pure compound eluted was the *dimethyl ester* of 3,6-*di*(*carboxymethylthio*)-1,2-*benzopyrene* (62 mg.), yellow needles, m. p. 113—115° (from ether) (Found: C, 67·8; H, 4·4; S, 13·7. $C_{26}H_{20}O_4S_2$ requires C, 67·8; H, 4·4; S, 13·9%), $\lambda_{max.}$ (in $CHCl_3$) 261, 272, 287, 299, 311, 353 (infl.), 376, 397, and 419 mμ (ε 35,520, 42,080, 23,280, 33,120, 37,200, 5000, 12,840, 27,200, and 34,520).

A sample (5 mg.) of the diester in acetic acid (2 ml.) was boiled under reflux and a solution of chromium trioxide (30 mg.) in acetic acid (2 ml.) was added dropwise. The progress of the oxidation was followed by thin-layer chromatography. When a fluorescent spot with R_F 0·85 (1,2-benzopyrene) no longer appeared, addition of chromium trioxide was stopped, and the solution was cooled, diluted with ether, and extracted with aqueous sodium carbonate. The ethereal solution was evaporated and the residue, dissolved in chloroform, was chromatographed on alumina. The sole product obtained had $\lambda_{max.}$ (in ether) 286, 297, 380, 400 (infl.), 424, and 454 mμ, as reported for 1,2-benzopyrene-3,6-dione,[22] and showed one spot (R_F 0·6) when chromatographed on a thin film. On thin-film chromatography, authentic 1,2-benzopyrene-1,6-dione had R_F 0·7. The crude product from oxidation of 1,2-benzopyrene, on thin-layer chromatography, showed spots with R_F 0·7 (1,6-dione), 0·6 (3,6-dione), and 0·5 (7-oxo-7*H*-benz[*de*]anthracene-3,4-dicarboxylic anhydride?).[23]

Reactions of Polycyclic Aromatic Hydrocarbons with Thioacetic Acid.—1,2-*Benzanthracene.* Ferrocene (20 mg.) and t-butyl hydroperoxide (1·8 g.) were added to 1,2-benzanthracene (1·0 g.) and thioacetic acid (5·5 ml.) in benzene (20 ml.), and the mixture was set aside for 3 hr. The products isolated by chromatography were sulphur (10 mg.), 1,2-benzanthracene (70 mg.), 10-acetylthio-1,2-benzanthracene (0·48 g.), and 9,10-di(acetylthio)-9,10-dihydro-1,2-benzanthracene (0·48 g.).

1,2-*Benzopyrene.* When 1,2-benzopyrene (0·42 g.) and thioacetic acid (2·5 ml.) in benzene (10 ml.) were treated with ferrocene (10 mg.) and t-butyl hydroperoxide (0·8 g.), the usual colour changes were observed but no heat was evolved. After 4 hr. the mixture was evaporated under reduced pressure. The residue (0·57 g.) when crystallised from benzene, gave yellow needles of crude 6-acetylthio-1,2-benzopyrene. On attempted chromatographic purification the thio-ester was converted into di-(1,2-benzopyren-6-yl) disulphide (0·15 g.), red plates, m. p. 278·5—280° (from chlorobenzene) (lit.,[24] 271—272°). Chromatography of the combined mother-liquors on neutral, deactivated alumina afforded a further quantity (0·20 g.) of 6-acetylthio-1,2-benzopyrene.

Pyrene. Ferrocene (10 mg.) and t-butyl hydroperoxide (1 g.) in benzene (5 ml.) were added to pyrene (0·5 g.) and thioacetic acid (3 ml.) in benzene (6 ml.). The mixture, which became warm and underwent the usual colour changes, was set aside for 4 hr. and then worked up in the usual way. The products were: sulphur (35 mg.), pyrene (0·13 g.), *di*-(1-*pyrenyl*) *disulphide* (90 mg.), m. p. 220—222° (Found: C, 82·3; H, 4·2; S, 13·4. $C_{32}H_{18}S_2$ requires C, 82·3; H, 3·9;

[22] Moriconi, Rakoczy, and O'Connor, *J. Org. Chem.*, 1962, **27**, 2772.
[23] Vollman, Becker, Correll, and Streeck, *Annalen*, 1937, **531**, 1.
[24] Wood and Fieser, *J. Amer. Chem. Soc.*, 1940, **62**, 2674.

S, 13·7%), 1-(*acetylthio*)*pyrene* (0·14 g.), m. p. 136—137·5° (Found: C, 77·6; H, 4·4; S, 11·7. $C_{18}H_{12}OS$ requires C, 78·2; H, 4·4; S, 11·6%), $\lambda_{max.}$ (in EtOH) 237, 245, 259, 269, 280, 306 (infl.), 319, 334, 349, 369, and 376 mμ (ε 35,200, 52,300, 12,550, 22,000, 35,900, 6250, 13,100, 26,400, 37,200, 1660, and 2260).

Perylene. When perylene (0·59 g.) in benzene (80 ml.) was treated in the usual way with thioacetic acid (3 ml.), t-butyl hydroperoxide (1·2 g.), and ferrocene (15 mg.), there was a rapid reaction and the mixture, which became first red then yellow during 5 min., was set aside overnight. Filtration gave a solid, which, on treatment with hot benzene, afforded perylene (0·1 g.). The residue, obtained by evaporation of the combined benzene filtrates, when fractionally crystallised from benzene, gave perylene (80 mg.) and a crude yellow compound (0·5 g.), which melted partially at 130 and completely at 160—167°. Repeated crystallisation of the latter from benzene gave 3,10-*di*(*acetylthio*)*perylene*, yellow needles, m. p. 232·5—237° (Found: C, 72·6; H, 4·2; S, 15·4. $C_{24}H_{16}O_2S_2$ requires C, 72·0; H, 4·0; S, 16·0%), $\lambda_{max.}$ (in $CHCl_3$) 256 (infl.), 260, 346 (infl.), 380 (infl.), 409, 433, and 461 mμ (ε 25,120, 31,320, 3200, 5240, 15,200, 30,080, and 36,720). A sample, when oxidised with chromium trioxide in acetic acid, afforded perylene-3,10-dione, identical with an authentic specimen.[25]

Preparation of Reference Compounds.—9-(*Phenylthio*)*anthracene.* 9-Bromoanthracene (10 g.) [26] was added to butyl-lithium prepared from 1-chlorobutane (10 g.) and lithium (1·2 g.) in ether (100 ml.). When formation of 9-anthryl-lithium [27] was complete (1 hr.), diphenyl disulphide (15 g.) was added and the mixture was boiled under reflux for 2 hr., and poured on to ice. Evaporation of the ethereal solution afforded an oily product which was separated, by chromatography on alumina and repeated crystallisation from methanol, into diphenyl disulphide, anthracene, and 9-(phenylthio)anthracene (3·5 g.), m. p. 100—102°.

1-(*Acetylthio*)*pyrene.* 1-Pyrenyl thiocyanate (2·0 g., prepared by reaction of pyrene with thiocyanogen [20]) and hydrated sodium sulphide (5 g.) were boiled in ethanol (25 ml.) under reflux for 1·5 hr. The solvent was evaporated *in vacuo*, the residue dissolved in aqueous sodium hydroxide, and the mixture filtered. Acidification of the filtrate afforded crude pyrene-1-thiol which was washed with water and heated with an excess of iodine in aqueous sodium hydroxide on a steam-bath for 1 hr. After cooling of the mixture, the product was washed with water, dried, and chromatographed on alumina (neutral, deactivated). The major fraction was di-(1-pyrenyl) disulphide, yellow prisms (1·2 g.), m. p. 220—222° (from benzene).

A large excess of zinc dust was added in small portions to a warm solution of the foregoing disulphide (1·0 g.) and sodium acetate (2 g.) in acetic anhydride (25 ml.), and the mixture was boiled under reflux for 2·5 hr., and filtered. The filtrate was evaporated under reduced pressure and the residue treated with water. The precipitate crystallised from benzene in pale yellow needles (1·1 g.) of 1-(acetylthio)pyrene, m. p. 136—137·5°.

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[25] Conrad-Billroth, *Z. phys. Chem.*, 1932, *B*, **15**, 1.
[26] Barnett and Cook, *J.*, 1924, 1084.
[27] Mikhailov and Chernova, *Doklady Akad. Nauk S.S.S.R.*, 1951, **78**, 489.