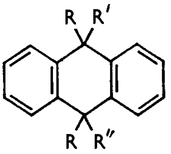
## 252. *Thiyl Radicals. Part I. Reactions of Anthracene with Oxygen and Thiols.*

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

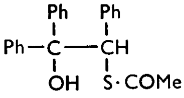
Anthracene reacts readily with thioacetic acid and oxygen, yielding 9,10-dihydro-9,10-di(acetylthio)anthracene and 9-(acetylthio)anthracene. Similar products are formed by reaction of anthracene and oxygen with thiobenzoic acid and with mercaptoacetic acid. With thiophenol and oxygen anthracene yields an unstable product formulated as a hydroperoxide, but the same reaction in the presence of acetic acid affords 9-phenylthioanthracene. Attempted reactions with toluene-ω-thiol and with dimercaptopropanol are described.

It is proposed that the reaction proceeds by free-radical chain addition, yielding a hydroperoxide which, in the presence of acids, is reduced to an alcohol and so converted into the final products by the usual ionic mechanism.

The reaction between anthracene, thioacetic acid, and oxygen was first described by Mikhailov and Blokhina [1] who observed that approximately one molar equivalent of the gas was rapidly absorbed and there were formed two isomeric 9,10-dihydro-9,10-di(acetylthio)anthracenes (I; R = H, R′ = R″ = Me•CO•S) and an unidentified yellow substance, m. p. 228—229°. 9,10-Dihydro-9,10-dimethyl-9,10-di(acetylthio)anthracene (I; R = Me, R′ = R″ = Me•CO•S) and 9,10-diethyl-9,10-dihydro-9,10-di(acetylthio)anthracene (I; R = Et, R′ = R″ = Me•CO•S) were produced from 9,10-dimethyl- and 9,10-diethylanthracene respectively by similar, though less rapid, reactions. In a later study [2] the same authors extended the reaction to 1,2-benzanthracene which yielded 9,10-dihydro-9,10-di(acetylthio)-1,2-benzanthracene, and to 9,9′-difluorenylidene and 9-benzylidenefluorene, both of which were converted into di(thiolacetates) by addition of $CH_3{\cdot}CO{\cdot}S$ groups across the exocyclic double bonds. Products of somewhat different types were obtained from 1,1,2-triphenylethylene, which yielded *S*-(2-hydroxy-1,2,2-triphenylethyl) thioacetate (II), and from anthracene and thioacetic acid in ether, which produced 9,10-dihydro-9-acetylthioanthracene (I; R = R′ = H, R″ = Me•CO•S).

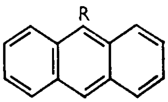


(I)



$Ph_2C(OH){\cdot}CHPh{\cdot}S{\cdot}COMe$

(II)



(III)

The structures of these products were not rigorously confirmed. The compounds obtained from anthracene were assigned the structure (I; R = H, R′ = R″ = Me•CO•S) on the basis of their oxidation to anthraquinone. No additional evidence was presented for the structures proposed for the products formed in reactions of substituted anthracenes.

The reaction mechanism originally put forward by Mikhailov and Blokhina [1] involved the addition across the reactive *meso*-positions of anthracene of two thioacetoxy-radicals formed by oxidation of thioacetic acid:

$$Me{\cdot}COSH + O_2 \longrightarrow Me{\cdot}COS{\cdot} + HO_2{\cdot}$$
$$Me{\cdot}COSH + HO_2{\cdot} \longrightarrow Me{\cdot}COS{\cdot} + H_2O_2$$

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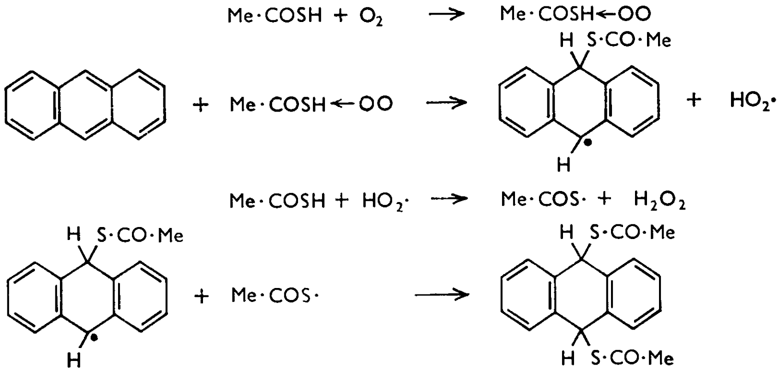
* Author's surname.

[1] Mikhailov and Blokhina, *Doklady Akad. Nauk S.S.S.R.*, 1951, **80**, 373.

[2] Mikhailov and Blokhina, *Problemy Mekhanizma Org. Reaktsii Akad. Nauk, Ukr. S.S.R.*; *Otdel. Fiz-Mat. i Khim. Nauk*, 1953, 215.

Later, the same authors,[2] aware that this mechanism accounts neither for the amount of oxygen absorbed nor for its rate of absorption, proposed a modified mechanism:



This mechanism is unsatisfactory: it does not account for the formation of 9,10-dihydro-9-(acetylthio)anthracene, and it involves an intermediate (Me•COS←OO) of a type never before described, for whose existence no direct evidence is offered.

These reactions show unusual features when compared with other free-radical reactions of anthracene. Thus, no bianthryl derivatives were isolated although attack of methyl,[3,4] benzyl,[4,5] 2-cyanopropyl,[6] phenyl,[4] and benzoylperoxy-radicals [7] on anthracene all lead to products of this type. Secondly, *meso*-disubstituted anthracenes, which usually do not readily undergo nuclear addition of free radicals,[8] reacted rapidly with thioacetic acid and oxygen. Finally, the thiol-catalysed dehydrogenation of 9,10-dihydroanthracene and its derivatives by azoisobutyronitrile [5,9] does not lead to products containing thio-groups although it involves the intermediate formation of free thiyl radicals.

With a view to resolve these inconsistencies we have now re-investigated the reaction of anthracene with thioacetic acid, and have extended it to other thiols. Similar reactions of substituted anthracenes have also been studied and will be described in Part II.

The main products from the reaction of anthracene with thioacetic acid and oxygen in benzene solution were the two isomeric 9,10-dihydro-9,10-di(acetylthio)anthracenes (I; R = H, R′ = R″ = Me•CO•S). These compounds, whose physical properties were similar to those described previously,[1] showed ultraviolet light absorption characteristic of substituted 9,10-dihydroanthracenes. The infrared spectra contained strong carbonyl bands, thus confirming the formation of a C–S bond between the aromatic nucleus and the mesomeric radical (Me•CO•S•⟷Me•CS•O•). Another major product was 9-(acetylthio)-anthracene (III; R = Me•CO•S), identified by comparison with a synthetic specimen. The close agreement between its properties and that of the reputed 9,10-dihydro-9-(acetylthio)anthracene [2] suggests that the two are identical: the analytical figures reported in the Russian work agree satisfactorily with those required by the fully aromatic compound. A fourth product, isolated in small yield, was di-(9-anthryl) disulphide; this appears to be identical with the unidentified yellow compound obtained by Mikhailov and Blokhina.[1]

When anthracene in benzene was treated under oxygen with other acidic compounds containing the SH group, similar reactions occurred. Thiobenzoic acid yielded both isomers of the addition product (I; R = H, R′ = R″ = Ph•CO•S), 9-(benzoylthio)-anthracene (III; R = Ph•CO•S), and a small amount of di-(9-anthryl) disulphide. The

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[3] Beckwith and Waters, *J.*, 1956, 1108.

[4] Norman and Waters, *J.*, 1957, 950.

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

[6] Bickel and Kooyman, *Rec. Trav. chim.*, 1952, **71**, 1137.

[7] Turner and Waters, *J.*, 1956, 879.

[8] Beckwith, Norman, and Waters, *J.*, 1958, 171; Engelsma, Farenhorst, and Kooyman, *Rec. Trav. chim.*, 1954, **78**, 878.

[9] Bickel and Kooyman, *Nature*, 1952, **170**, 211.

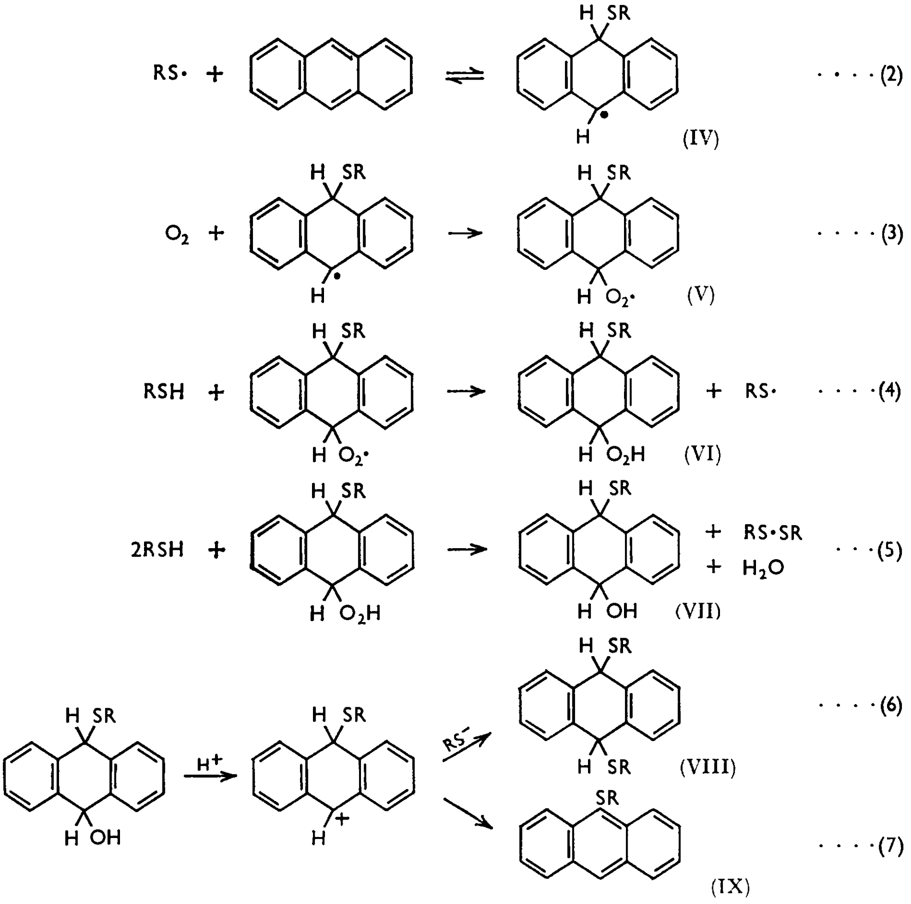
major product from reaction of anthracene in benzene with mercaptoacetic acid and oxygen was 9,10-di(carboxymethylthio)-9,10-dihydroanthracene (I; $R = H$, $R' = R'' = S{\cdot}CH_2{\cdot}CO_2H$) of which only one isomer was isolated. Because of its instability and its insolubility, the dicarboxylic acid could not be obtained analytically pure, but its structure was confirmed by its conversion into the dimethyl ester (I; $R = H$, $R' = R'' = S{\cdot}CH_2{\cdot}CO_2Me$), and into the known (9-anthrylthio)acetic acid (III; $R = S{\cdot}CH_2{\cdot}CO_2H$). The same reaction in alcohol yielded an unstable acid which on attempted purification was converted into anthraquinone.

With toluene-ω-thiol and oxygen, anthracene in benzene reacted slowly; the products were difficult to isolate and anthraquinone and unchanged anthracene were the only pure compounds obtained. The reaction with dimercaptopropanol was very similar. Anthraquinone was also produced in the analogous reaction with thiophenol, but the principal product was a white powder, insoluble in benzene, which decomposed vigorously when kept at room temperature.

In all of these experiments the rate of oxygen absorption decreased during the reaction. The oxygen-absorption curves were not accurately reproducible but all had a similar shape. In some cases there was an induction period of variable duration, but the absorption of oxygen could invariably be initiated by the addition of free-radical sources such as ferrous ion and cumene hydroperoxide.

To account for these experimental observations we propose the following reaction mechanism:

$$RSH + O_2 \longrightarrow RS\cdot + HO_2\cdot \qquad \ldots\ldots(1)$$

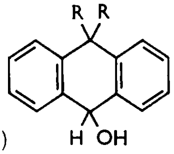


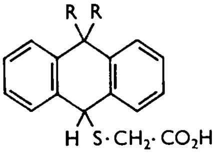
The first steps (1—4), which are analogous to the reactions of olefins and of indene with thiols and oxygen,[10] account for the observation that the rate of oxygen absorption is proportional to the amount of anthracene present. It is suggested that with weakly acidic thiols the reaction proceeds no further and the products obtained are hydroperoxides (VI) or compounds resulting from their decomposition. We suggest that the unstable solid produced in the reaction of anthracene with thiophenol was the hydroperoxide (VI; R = Ph), and that the anthraquinone resulting from reactions with toluene-ω-thiol, with dimercaptopropanol, and with mercaptoacetic acid in alcohol was formed from similar hydroperoxides.

In the presence of acidic thiols the intermediate hydroperoxide is converted into addition and substitution products by the reactions (5—7). The feasibility of this mechanism has been demonstrated by treatment of cumene hydroperoxide with mercaptoacetic acid in benzene, (cumylthio)acetic acid being produced. Additional evidence was provided by reaction of 10,10-dibenzyl-9,10-dihydro-9-hydroxyanthracene (X; R = $CH_2Ph$) with mercaptoacetic acid, whereby the substituted acid (XI; R = $CH_2Ph$) was obtained. When 9,10-dihydro-9-hydroxyanthracene (X; R = H) was treated with mercaptoacetic acid, anthracene and 9-carboxymethylthio-9,10-dihydroanthracene (XI; R = H) were produced, thus providing analogies for the formation of both substitution (IX) and addition (VIII) products from intermediates of the type (VII). Finally, the reaction of anthracene with thiophenol and oxygen was repeated in the presence of acetic acid. As predicted by the above mechanism there was no unstable hydroperoxide formed and the only product isolated was 9-(phenylthio)anthracene.

The above mechanism is compatible with the formation of *S*-(2-hydroxy-1,2,2-triphenylethyl) thioacetate (II) from thioacetic acid and oxygen with 1,1,2-triphenylethylene as reported by Mikhailov and Blokhina.[2] It also accounts for some of the unusual features of these reactions mentioned above. Thus, the absence of dimeric products may be attributed to the high concentration of oxygen, which acts as a scavenger for radicals of type (IV). By analogy with the mechanism for the free-radical addition of thiols to olefins [11] it is probable that reaction (2) is reversible. Under the more vigorous conditions employed for thiol-catalysed dehydrogenation of 9,10-dihydroanthracenes the equilibrium presumably favours the dissociation of (IV) to such an extent that formation of the addition product (VIII) cannot occur.

(X)





(XI)

Reactions of thiols with aromatic compounds in the presence of oxygen may have biological significance. The premercapturic acids produced by metabolic oxidation of aromatic compounds [12] are known to have structures similar to, but of different orientation from, the intermediate (VII). Further, it is believed that metabolic hydroxylation of aromatic molecules involves reactions utilising a thiol and molecular oxygen, and is catalysed by ferrous ion.[13] Other reactions of polycyclic aromatic hydrocarbons with cell constituents containing the thiol group also appear possible. The above mechanism could account for the cross-linking of proteins, or for the irreversible binding of aromatic compounds to skin protein.[14] Interference with cell hydrogen-transfer processes by

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[10] Oswald, *J. Org. Chem.*, 1959, **24**, 443; Ford, Pitkethly, and Young, *Tetrahedron*, 1958, **4**, 325.

[11] Walling and Helmreich, *J. Amer. Chem. Soc.*, 1959, **81**, 1144.

[12] Boyland and Sims, *Biochem. J.*, 1958, **68**, 440; Knight and Young, *ibid.*, 1958, **70**, 111.

[13] Mitoma, Posner, Reitz, and Udenfriend, *Arch. Biochem. Biophys.*, 1956, **61**, 431; Mason, *Adv. Enzymology*, 1957, **19**, 177.

[14] Miller, *Cancer Res.*, 1951, **11**, 100; Bhargava, Hadler, and Heidelberger, *J. Amer. Chem. Soc.*, 1955, **77**, 2877; Bhargava and Heidelberger, *ibid.*, 1956, **78**, 3671.

reactions of such thiols as glutathione or reduced thioctic acid with aromatic hydrocarbons may also occur.

Compounds required for reference or as starting materials were prepared by standard methods. 9,10-Dihydro-9-hydroxyanthracene (X; R = H) and 10,10-dibenzyl-9,10-dihydro-9-hydroxyanthracene (X; R = $CH_2Ph$) were produced by reduction of anthrone and 10,10-dibenzylanthrone respectively with lithium aluminium hydride, 9-(acetoxythio)-anthracene was prepared by reductive acetylation of di-(9-anthryl) disulphide, and (cumylthio)acetic acid resulted from the acid-catalysed addition of mercaptoacetic acid to α-methylstyrene.

## EXPERIMENTAL

Ultraviolet absorption spectra were determined in ethanol, unless otherwise stated, on an Optica recording spectrophotometer. Adsorption chromatography was conducted on acid-washed alumina, hexane and hexane–benzene being used as eluants. Microanalyses were carried out by the C.S.I.R.O. and University of Melbourne Microanalytical Service.

*Reaction of Anthracene with Thioacetic Acid.*—A suspension of anthracene (5 g.) in thioacetic acid (20 ml.; b. p. 91—94°) and benzene (50 ml.) was shaken under oxygen at room temperature. Oxygen absorption was slow and became negligible after 7·5 hr. Unchanged anthracene (2·4 g.) was removed by filtration, and the solvent and excess of thioacetic acid were evaporated under a reduced pressure of nitrogen. When the residue was treated with methanol (50 ml.) a yellow solid was obtained, which on fractional crystallisation from methanol yielded anthracene (1 g.) and 9-(acetylthio)anthracene, m. p. and mixed m. p. 145—146°. The material obtained by evaporation of the mother-liquors when fractionally crystallised from hexane yielded sulphur (20 mg.), 9-(acetylthio)anthracene (total yield, 1·6 g.), and one isomer of 9,10-dihydro-9,10-di(acetylthio)anthracene (0·4 g.) which formed rods, m. p. 124·5—126° (Found: C, 66·1; H, 5·1; S, 19·9. Calc. for $C_{18}H_{16}O_2S_2$: C, 65·8; H, 4·9; S, 19·5%), $\lambda_{max.}$ 2547 Å (ε 10,810).

In a second experiment conducted under identical conditions there was a long induction period followed by rapid absorption of oxygen (550 ml.) during 2 hr. The crude product was isolated as before and separated into its constituents by chromatography on alumina. The products were 9-(acetylthio)anthracene, di-(9-anthryl) disulphide, m. p. 218—222°, and a second isomer of 9,10-dihydro-9,10-di(acetylthio)anthracene, which crystallised from hexane in rods, m. p. 145—147° (Found: C, 65·6; H, 5·0; S, 19·9%), $\lambda_{max.}$ 2360 Å (ε 17,080). All anthracene derivatives containing the acetylthio-group showed strong infrared carbonyl absorption at 1685—1695 $cm.^{-1}$.

*Reaction of Anthracene with Thiobenzoic Acid.*—When anthracene (18 g.) thiobenzoic acid (7 g.), and benzene (25 ml.) were shaken together under oxygen there was an initial rapid absorption of gas (*ca.* 90 ml. in 10 min.) but the reaction soon ceased and was then re-initiated by the addition of small amounts of cumene hydroperoxide and ferrous sulphate. After a total of 276 ml. of oxygen had been absorbed the mixture was washed with water and sodium carbonate solution and evaporated under a reduced pressure of nitrogen. Attempts to separate the residue into the pure components by crystallisation having failed, it was chromatographed on alumina. The following compounds were obtained: (i) anthracene (0·5 g.); (ii) di-(9-anthryl) disulphide (10 mg.); (iii) one *isomer* of 9,10-*dihydro*-9,10-*di*(*benzoylthio*)*anthracene* (0·5 g.), which crystallised from hexane–benzene in plates, m. p. 202—204° (Found: C, 74·5; H, 4·3; S, 13·9. $C_{28}H_{20}O_2S_2$ requires C, 74·3; H, 4·45; S, 14·2%), $\lambda_{max.}$ (in cyclohexane) 2390 (ε 37,000) and 2773 Å (ε 19,400); (iv) a second *isomer* (0·2 g.), which crystallised from hexane–benzene in prisms, m. p. 193·5—195·5°, mixed m. p. with the other isomer *ca.* 170° (Found: C, 74·6; H, 4·6; S, 13·7%), $\lambda_{max.}$ (in cyclohexane) 2390 (ε 31,410) and 2731 Å (ε 17,700); (v) 9-(*benzoylthio*)*anthracene* (0·2 g.), which crystallised from benzene–hexane in yellow prisms, m. p. 222—224° (Found: C, 80·1; H, 4·62; S, 10·1. $C_{21}H_{14}OS$ requires C, 80·2; H, 4·5; S, 10·2%), $\lambda_{max.}$ 3570 (ε 10,800), 3747 (ε 15,440), and 3950 Å (ε 13,380).

*Reaction of Anthracene with Mercaptoacetic Acid.*—(*a*) Anthracene (5 g.), mercaptoacetic acid (21 g.), and benzene (50 ml.) were shaken together under oxygen. When the initial rapid absorption of oxygen (660 ml. in 75 min.) had ceased, the mixture was extracted with aqueous sodium carbonate, and the extract was washed with ether and acidified with hydrochloric acid. The yellow precipitate was collected, washed, and treated with hot acetone. Crystallisation of the insoluble material from *NN*-dimethylformamide yielded plates (2·8 g.), m. p. 218—220°, of 9,10-*di*(*carboxymethylthio*)-9,10-*dihydroanthracene* (Found: C, 59·0; H, 4·7; S, 17·8. $C_{18}H_{16}O_4S_2$ requires C, 60·0; H, 4·5; S, 17·8%). The ultraviolet spectrum showed an inflexion at 2507 Å (ε 3660). The acetone-soluble material (2 g.) yielded a further quantity (1·8 g.) of the diacid on treatment with warm acetic acid. Esterification of the dicarboxylic acid with diazomethane yielded the *dimethyl ester*, which crystallised from ether in plates, m. p. 99—101·5° (Found: C, 61·7; H, 5·2; S, 16·6. $C_{20}H_{20}O_4S_2$ requires C, 61·8; H, 5·2; S, 16·5%).

When a suspension of the dicarboxylic acid (0·33 g.) in acetic acid (5 ml.) and hydrochloric acid (0·5 ml.) was heated a clear solution was rapidly obtained. Dilution with water yielded a precipitate of (9-anthrylthio)acetic acid (0·2 g.), which crystallised from ether–hexane in pale yellow needles, m. p. 166—167° (lit.,[15] m. p. 164°) (Found: C, 72·0; H, 4·7. Calc. for $C_{16}H_{12}O_2S$: C, 71·6; H, 4·5%), $\lambda_{max.}$ 2517 (ε 82,390), 3410 (ε 3040), 3557 (ε 4673), 3733 (ε 8519), and 3937 Å (ε 7560).

(*b*) A mixture of anthracene (0·9 g.), mercaptoacetic acid (5 ml.), and ethanol (20 ml.), when shaken under oxygen, absorbed gas very rapidly (total: 322 ml. in 1·6 hr.). Filtration then afforded anthraquinone (0·15 g.), and a further quantity (0·15 g.) of the same compound was obtained when the filtrate was evaporated and the residue treated with methanol. The methanol-soluble material was a red viscous liquid which dissolved readily in aqueous alkali. When it was reprecipitated with acid, however, it was converted in part into anthraquinone; no other product was isolated.

*Reaction of Anthracene with Thiophenol.*—(*a*) A mixture of anthracene (2·7 g.), thiophenol (10 ml.), and benzene was shaken under oxygen. Absorption of gas was initiated by the addition of small amounts of cumene hydroperoxide and ferrous sulphate, and was virtually complete after 7 hr. (total 340 ml.). A fine, white, insoluble powder (2 g.) which had slowly accumulated in the reaction mixture was filtered off and washed with benzene. When kept in air it rapidly became hot and decomposed to a dark brown resin (*A*). The filtrate was washed with aqueous sodium hydroxide to remove unchanged thiophenol, dried, and evaporated to 20 ml. under reduced pressure. After dilution with hexane the mixture was chromatographed on alumina. The first fraction was a mixture and was further resolved by repeated chromatography and fractional crystallisation. In this way there were obtained: (i) diphenyl disulphide (1·6 g.); (ii) a compound formulated as 9-(*phenylthio*)*anthracene*, which crystallised from hexane in yellow prisms (50 mg.), m. p. 100·5—102° (Found: C, 83·9; H, 4·9; S, 11·2. $C_{20}H_{14}S$ requires C, 83·9; H, 4·9; S, 11·2%), $\lambda_{max.}$ 2512 (ε 88,000), 2571 (ε 112,000), 3427 (ε 3726), 3585 (ε 5505), 3756 (ε 7551), and 3965 Å (ε 6850); (iii) yellow crystals (0·3 g.), m. p. 132·5—135° (Found: C, 86·6; H, 5·2; S, 8·5%), which could not be further purified (see next experiment.) Other fractions from the first chromatographic separation included anthraquinone (0·55 g.) and traces of highly coloured polar substances.

The decomposition product (*A*), when dissolved in hexane–benzene and chromatographed, yielded anthracene and anthraquinone as the only identifiable products.

A second experiment under identical conditions yielded the same insoluble product, which again rapidly decomposed although it was immediately transferred to a vacuum-desiccator.

(*b*) Anthracene (2·6 g.), thiophenol (10 ml.), acetic acid (10 ml.), and benzene (30 ml.) were shaken under oxygen. Absorption of oxygen (260 ml.) ceased after 6 hr. and the mixture was then filtered to remove unchanged anthracene (0·36 g.). The filtrate was washed with aqueous sodium hydroxide, dried, and evaporated under a reduced pressure of nitrogen. When the residue was treated with hot hexane (70 ml.) there remained an insoluble material (0·2 g.) which was separated into anthracene and anthraquinone. The hexane-soluble material was separated by chromatography on alumina into diphenyl disulphide (3·27 g.) and a yellow mixture (0·75 g.), m. p. *ca.* 125°. When the latter was heated under reduced pressure, diphenyl disulphide, anthracene, and a yellow substance, m. p. 130°, sublimed. The residue consisted of 9-(phenylthio)anthracene which crystallised from hexane in plates, m. p. 100·5—102°.

*Reaction of Anthracene with Toluene-ω-thiol.*—The thiol (10 ml.) was added to a suspension of anthracene (2·7 g.) and ferrous sulphate (50 mg.) in benzene (30 ml.), and the mixture shaken under oxygen. Absorption of gas was very slow (100 ml. in 11 hr.). The mixture was filtered from unchanged anthracene (1·3 g.). The filtrate was washed, dried, and evaporated under reduced pressure. When the residue was chromatographed on alumina the only identifiable compounds were anthracene (0·45 g.) and anthraquinone (90 mg.).

[15] Friedlander and Simon, *Ber.*, 1922, **55**, 3969.

*Reaction of Anthracene with* 2,3-*Dimercaptopropanol.*—Addition of a small amount of ferrous sulphate initiated the absorption of oxygen by a mixture of anthracene (1·0 g.), 2,3-dimercaptopropanol (5 ml.), and benzene (30 ml.). After the absorption of 180 ml. of gas, the benzene solution was pale yellow, and a yellow, viscous precipitate had formed. When a drop of the benzene solution was chromatographed on acetylated paper three constituents were detected; two of these, anthracene (0·01 g.) and anthraquinone (0·1 g.) were separated by fractional crystallisation, but the third could not be isolated. The viscous precipitate, which resisted purification by crystallisation, was acetylated and chromatographed on alumina. The only identifiable fractions were anthracene (0·02 g.) and anthraquinone (0·05 g.).

*Reaction of Cumene Hydroperoxide with Mercaptoacetic Acid.*—A solution of cumene hydroperoxide (1·0 g.) and mercaptoacetic acid (3 ml.) in benzene (10 ml.) was stored under nitrogen for 2 weeks, then shaken with sodium carbonate solution, and the alkaline extract was washed with ether, acidified with hydrochloric acid, and set aside in the refrigerator. There was deposited (αα-dimethylbenzylthio)acetic acid (0·72 g.), which recrystallised from hexane in needles, m. p. and mixed m. p. 69·5—70·5°.

When a similar mixture of reactants was shaken under oxygen for 5 days no absorption of gas was observed. Isolation of the product as above yielded only the same acid product (0·34 g.).

*Reaction of* 9,9-*Dibenzyl*-9,10-*dihydro*-10-*hydroxyanthracene with Mercaptoacetic Acid.*—The substituted hydroxyanthracene was prepared as follows: 10,10-Dibenzylanthrone (4 g.) and lithium aluminium hydride (0·15 g.) in ether (30 ml.) were refluxed for 1·8 hr. and the excess of anhydride was then destroyed by addition of ethyl acetate. When the mixture was shaken with dilute sulphuric acid, a precipitate of 9,9-dibenzyl-9,10-dihydro-10-hydroxyanthracene was formed, and a further quantity was obtained by evaporation of the ethereal solution. The hydroxy-compound crystallised from benzene in prisms (2·8 g., 70%), m. p. 174—177°.

When a solution of the foregoing hydroxy-compound (1·3 g.) and mercaptoacetic acid (5 ml.) in benzene (17 ml.) was kept under nitrogen for 3 days a crystalline precipitate (0·25 g.) of (9,9-*dibenzyl*-9,10-*dihydro*-10-*anthrylthio*)*acetic acid* was slowly formed. After filtration, the benzene solution was washed thrice with aqueous sodium carbonate, and the extract was acidified. The precipitated acid (0·63 g.) was collected, combined with that previously obtained, and crystallised from benzene, whence it formed needles, m. p. 208—210° (Found: C, 80·3; H, 5·9; S, 6·9. $C_{30}H_{26}O_2S$ requires C, 80·0; H, 5·8; S, 7·1%).

*Reaction of* 9,10-*Dihydro*-9-*hydroxyanthracene with Mercaptoacetic Acid.*—(*a*) A mixture of anthrone (2·0 g.), lithium aluminium hydride (0·2 g.), and ether (150 ml.) was stirred at room temperature for 1½ hr. and was then poured directly on to mercaptoacetic acid (10 ml.), kept overnight, and treated with dilute sulphuric acid. The aqueous portion was discarded, and the ethereal solution extracted with sodium carbonate solution. The alkaline extract was washed with ether and acidified. The precipitate of 9-*carboxymethylthio*-9,10-*dihydroanthracene* (0·50 g.) crystallised from benzene–hexane in plates, m. p. 147—149° (Found: C, 71·0; H, 5·3; S, 12·4. $C_{16}H_{14}O_2S$ requires C, 71·1; H, 5·2; S, 11·9%), $\lambda_{max.}$ 2129 (ε 22,300), 2521 (ε 1525), 2660 (ε 1300), and 2751 Å (ε 1065). Evaporation of the ethereal solution yielded anthracene (0·32 g.).

(*b*) Anthrone (4 g.) was reduced with lithium aluminium hydride (0·4 g.) in ether (200 ml.). The mixture was treated with aqueous sodium hydroxide, and the ether layer was separated, washed, dried, and evaporated under a reduced pressure of nitrogen. The residue of 9,10-dihydro-9-hydroxyanthracene crystallised from light petroleum in fine needles (2·0 g.), m. p. 74° (lit.,[16] m. p. 76°). A solution of the foregoing hydroxy-compound (1·0 g.) and mercaptoacetic acid (10 ml.) in ether (25 ml.) was stored under nitrogen for 28 hr. Anthracene (80 mg.) was precipitated from the mixture and was collected. Extraction of the mixture with sodium carbonate solution yielded 9-carboxymethylthio-9,10-dihydroanthracene (0·22 g.). Anthracene (0·21 g.) was obtained by evaporation of the residual ethereal solution.

*Preparation of Reference Compounds.*—*Di*-(9-*anthryl*) *disulphide.* Anthracene was converted into 9-mercaptoanthracene *via* the dithio-chloride.[15] The crude thiol was dissolved in aqueous sodium hydroxide and oxidised to the disulphide with iodine. Di-(9-anthryl) disulphide crystallised from benzene in orange prisms, m. p. 218—222° (Found: C, 80·15; H, 4·4; S, 15·6. Calc. for $C_{28}H_{18}S_2$: C, 80·4; H, 4·3; S, 15·3%).

9-(*Acetylthio*)*anthracene.* Zinc dust (3·5 g.) was added in small portions to a warm mixture of di-(9-anthryl) disulphide (1·7 g.), sodium acetate (1 g.), and acetic anhydride (15 ml.). The

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[16] von Perger, *J. prakt. Chem.*, 1881, **23**, 137.

mixture was boiled for 5 min., filtered whilst hot, and diluted with water. The precipitate of 9-(*acetylthio*)*anthracene* was collected, washed with water, and crystallised from hexane, forming yellow prisms (1·1 g., 54%), m. p. 146—147° (Found: C, 76·4; H, 4·9; S, 12·7. $C_{16}H_{12}OS$ requires C, 76·2; H, 4·8; S, 12·7%), $\lambda_{max.}$ 2487 ($\varepsilon$ 82,680), 3557 ($\varepsilon$ 5395), 3739 ($\varepsilon$ 7597), and 3939 Å ($\varepsilon$ 6200).

(*αα-Dimethylbenzylthio*)*acetic acid*. Concentrated sulphuric acid (5·0 ml.) was added dropwise with stirring to α-methylstyrene (5·0 g.) and mercaptoacetic acid (10 ml.) in acetic acid (25 ml.). After the addition the warm solution was set aside for 2 hr., then diluted with water, and extracted with ether. The ethereal solution was washed with water and extracted with aqueous potassium hydroxide. The oily precipitate of the required acid, which was formed on acidification of the alkaline extract, solidified on cooling. It crystallised from hexane in rods (7·2 g., 80%), m. p. 70—71° (Found: C, 63·1; H, 6·8; S, 15·5. Calc. for $C_{11}H_{14}O_2S$: C, 62·9; H, 6·7; S, 15·2%).

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