

Reaction of Some Triarylmethyl Radicals, Polyaryllkenes, and 9,10-Dihydro-9,10-epidioxyanthracenes with Sulphur Dioxide; Detection of Radicals and/or Cations derived from the Corresponding Cation Radicals

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The reactions of some triarylmethyl radicals, polyaryllkenes, and 9,10-dihydro-9,10-epidioxyanthracene derivatives with sulphur dioxide have been investigated. In these reactions radicals and/or cations, possibly derived from the corresponding cation radicals, were detected by e.s.r. and u.v. spectroscopy. In the reactions of 9,10-dihydro-9,10-epidioxyanthracene derivatives with conc. sulphuric acid or antimony pentachloride, cation radicals of the anthracene derivatives were detected. Oxidation of stable radicals with sulphur dioxide was also investigated.

OXIDATION of the side-chain of alkylbenzenes has been effected by anodic oxidation,¹ or by metal^{2,3} or other chemical oxidants;⁴ the proposed mechanism involves initial one-electron transfer to give the cation radical of the alkylbenzene followed by irreversible proton loss to give a benzyl radical, the latter being generally more easily oxidizable than the corresponding alkylbenzene.¹ In these reactions cation radicals of polyalkylbenzenes have been observed by e.s.r. and u.v. spectroscopy,³⁻⁵ but the presence of benzyl radicals, which would strongly support this proposed mechanism, has not been detected. The formation of the tropylium ion *via* electron transfer from cycloheptatriene to a cation radical⁶ or to an arylmethyl cation⁷ has been reported, but a mechanism involving hydrogen loss from the cycloheptatriene cation radical to afford the tropylium ion was suggested.

Recently we reported a novel preparation of cation radicals of anthracene derivatives from the corresponding peroxides in sulphur dioxide.⁸ Sulphur dioxide was also found to act as an oxidant, and electron-rich alkenes give the corresponding cation radicals in this medium.⁹ In the light of these results, we have examined the reactions of 9,10-dihydro-9-methyl-10-phenyl-9,10-epidioxyanthracene derivatives and some alkenes with sulphur dioxide, and attempted to detect the presence of radicals and/or cations derived from cation radicals. Tris-(biphenyl-4-yl)methyl is known to be oxidized by sulphur dioxide to tris(biphenyl-4-yl)methyl cation.¹⁰ In the presence of oxygen triphenylmethyl also affords the corresponding methyl cation with sulphur dioxide.¹¹ To investigate this type of reaction in more detail, we have examined the reactions of some stable radicals with sulphur dioxide in the presence or absence of oxygen.

RESULTS AND DISCUSSION

Oxidation of Stable Radicals with Sulphur Dioxide.—When tris(biphenyl-4-yl)methyl (1) was dissolved in

sulphur dioxide in the absence of oxygen, the tris-(biphenyl-4-yl)methyl cation was formed. The rate of oxidation was roughly estimated by following the change in intensity of the e.s.r. signal due to (1). On addition of ethanol, ethyl tris(biphenyl-4-yl)methyl ether (7) was obtained (Table 1). A similar reaction was observed with tris(*p*-*t*-butylphenyl)methyl (2), which gave the corresponding ether (8).

TABLE I

Oxidation of stable radicals with sulphur dioxide^a

Radicals	$\tau_{1/2}/h$ ^b	U.v. absorption of cation/nm ^c	Product and % yield
(1) ^d	0.6	540	(7) 70
(2) ^e	30	445	(8) 75
(3) ^{f,g}	0	455	(17) 90
(4) ^h	1.5	780 ⁱ	(10) 85
(5) ^{j,k}	0	820 ^k	(16) 70
(6) ^{l,m}	44 ^m	795	(14) 90

^a Reactions of the radicals with sulphur dioxide were performed at room temperature in the dark for 72 h; ethanol was then added to the solution. ^b The half-life of the radical was estimated by measuring the e.s.r. signal periodically. ^c Obtained by dissolving the corresponding chlorides or bromide in sulphur dioxide. ^d A. H. Maki, R. D. Allendoefer, J. C. Danner, and R. T. Keys, *J. Amer. Chem. Soc.*, 1968, **90**, 4225. ^e W. J. van der Hart, *Mol. Phys.*, 1970, **19**, 75. ^f M. T. Johns, *J. Chem. Phys.*, 1961, **35**, 1146. ^g Oxygen was added to a solution of the radical in sulphur dioxide. ^h $a_H(4) = 3.5$ mT. ⁱ $\log \epsilon = 4.07$. ^j $a_H(4) = 3.7$ mT, $a_H(4) = 0.8$ mT. ^k $\log \epsilon = 4.08$. ^l R. Kuhn and F. A. Neugebauer, *Monatsh.*, 1964, **95**, 3. ^m Estimated by measuring the u.v. spectrum periodically.

(9-Anthryl)diphenylmethyl (4) was also oxidized in the absence of oxygen, and the ethoxysulphonyl compound (10) was isolated as the sole product. A solution in sulphur dioxide of the ethoxy-compound (11) also gave (10), suggesting that ethyl sulphite anion acts as a nucleophile in this system. Although nucleophilic substitution with sulphite ion at positive carbon provides

⁶ P. Beresford and A. Ledwith, *Chem. Comm.*, 1970, 15.

⁷ M. Ballester, J. Riera-Figueras, J. Castaner, and A. Rodrigues-Siurana, *Tetrahedron Letters*, 1971, 2079.

⁸ N. Kakeya, M. Nojima, and N. Tokura, *J.C.S. Perkin I*, 1976, 87.

⁹ M. Nojima, G. Nagao, N. Kakeya, M. Takagi, and N. Tokura, *J.C.S. Chem. Comm.*, 1976, 486.

¹⁰ W. Schlenk, T. Weickel, and A. Herenstein, *Annalen*, 1910, **372**, 1.

¹¹ H. Takeuchi, T. Nagai, and N. Tokura, *Bull. Chem. Soc. Japan*, 1970, **43**, 1747.

¹ V. D. Parker and R. N. Adams, *Tetrahedron Letters*, 1969, 1721.

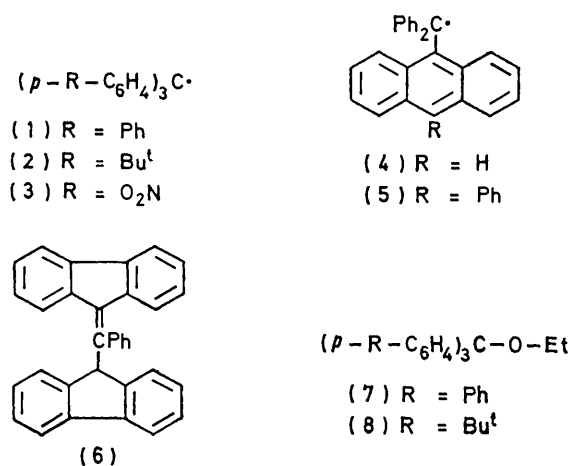
² E. I. Heiba, R. N. Dessau, and W. J. Koel, *J. Amer. Chem. Soc.*, 1969, **91**, 6830.

³ J. K. Kochi, R. T. Tang, and T. Bernath, *J. Amer. Chem. Soc.*, 1973, **95**, 7114.

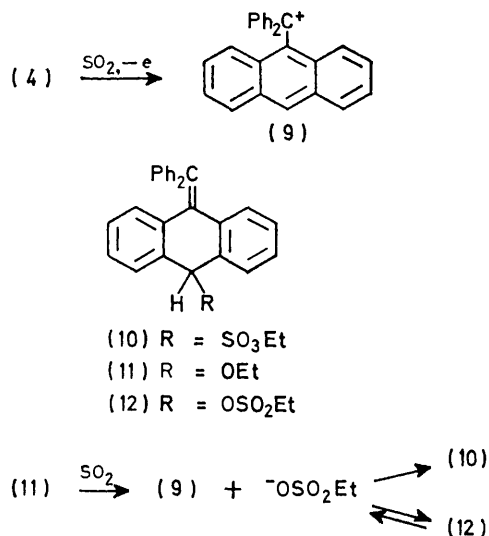
⁴ J. K. Kochi, *Tetrahedron Letters*, 1975, 41; however, see also, E. Baccocchi and G. Illuminati, *ibid.*, p. 2265.

⁵ U. Svanholm and V. D. Parker, *J. Amer. Chem. Soc.*, 1976, **8**, 2942, and references therein.

sulphites rather than sulphonates,^{12,13} the expected sulphite (12) was not detected in the above reactions.



We suggest the mechanism in Scheme 1 to explain the formation of (10). The first step involves the formation of (11) from (9) and ethanol, which is followed by cleavage of the C-O bond of (11) by sulphur dioxide, a weak Lewis acid,^{8,12} to afford (9) and ethyl sulphite anion. The C-O bond of (12), if formed, would be expected to be broken more easily than that of (11),¹⁴ giving (9) and ethyl sulphite anion. As a result, the ethyl sulphonate (10) formed by attack of the sulphur atom of ethyl sulphite ion on the positive carbon of (9)

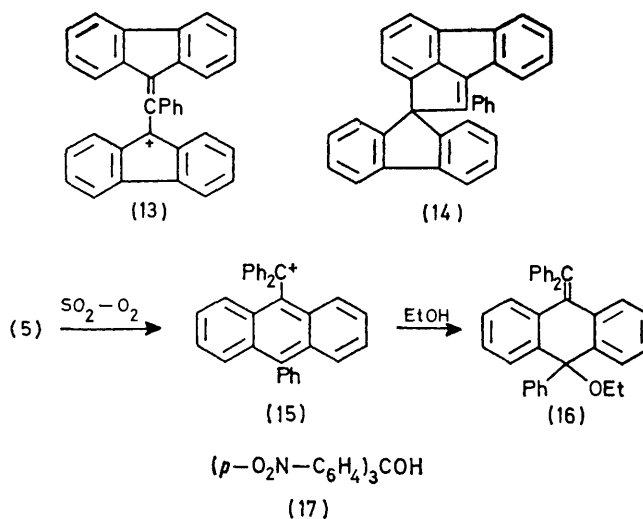


SCHEME 1

is the sole isolable product in this system. Because of steric reasons, the carbon centre of the triarylmethyl cation does not seem to be attacked by the bulky

ethyl sulphite ion to form the corresponding ethyl sulphonate.^{15,16}

9-(α -Fluorenyl-ylidenebenzyl)fluorenyl (6), which is known to be one of the most stable radicals, can only be oxidized with sulphur dioxide in the presence of oxygen. The reaction was followed by u.v. spectroscopy [(6) shows an absorption maximum at 490 nm]. Although an absorption maximum due to the cation (13) was not observed, the spiro-compound (14), which we consider to be obtained from this cation by intramolecular cyclization, was obtained quantitatively. The reaction of 9-(α -fluorenyl-ylidenebenzyl)fluorenyl chloride in sulphur dioxide also afforded (14). The (phenylanthryl)methyl (5) was also oxidized to the



corresponding cation (15) in the presence of oxygen; reaction with ethanol then gave the ethoxy-compound (16). The behaviour of tris-(*p*-nitrophenyl)methyl (3) in sulphur dioxide seems to be different from that of the other radicals. In the presence of oxygen the e.s.r. signal of the radical disappeared rapidly, but a u.v. absorption due to the corresponding cation was not detected. After work-up with ethanol tris-(*p*-nitrophenyl)methanol (17) was obtained rather than the expected ether. In other solvents the radical (3) reacts with oxygen to afford a symmetrical peroxide.¹⁷

In conclusion, fairly stable radicals, from which stable cations are obtained, are oxidized by sulphur dioxide in the absence of oxygen, but extremely stable radicals require the presence of oxygen also.

Reactions of 9,10-Dihydro-9-methyl-10-phenyl-9,10-epidioxyanthracene Derivatives with Sulphur Dioxide.—When the dihydroepidioxyanthracene (18) was treated with degassed sulphur dioxide in the dark, the formation of the neutral radical (5) only was observed, even in the

¹² M. M. Rogic, K. P. Klein, J. M. Balquist, and B. C. Oxenrider, *J. Org. Chem.*, 1976, **41**, 482.

¹³ G. Hesse and S. Majumdar, *Chem. Ber.*, 1960, **93**, 1129.

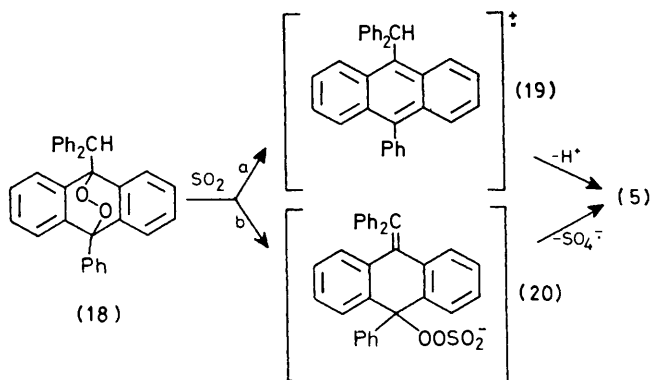
¹⁴ M. Nojima, F. Shiba, and N. Tokura, *Chem. Letters*, 1972, 1137.

¹⁵ J. A. Hirsch, 'Topics in Stereochemistry,' vol. 1, eds. N. L. Allinger and E. L. Eliel, Wiley, New York, 1967, p. 199.

¹⁶ R. Heck, P. S. Magee, and S. Winstein, *Tetrahedron Letters*, 1964, 2033.

¹⁷ A. Hantzsch and F. Hein, *Ber.*, 1919, **52**, 495.

first step of the reaction; the intensity of the e.s.r. signal due to (5) increased during 24 h, and then remained



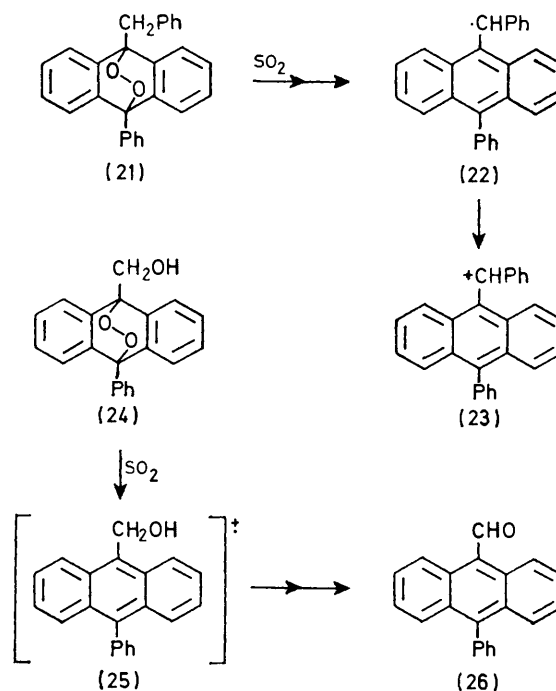
unchanged for a week. This result suggests slow formation of the cation radical (19) with rapid loss of a proton to afford (5) (path a). However an alternative path (b) may be considered to explain this result; concerted cleavage of the C-O bond and deprotonation may occur to form the intermediate (20), followed by elimination of SO_4^- to give (5). It is difficult to decide which path (a or b in Scheme 2) is more probable in this reaction. Introduction of oxygen into this solution caused the oxidation of (5) to the cation (15), which reacted with ethanol giving (16) in 34% yield. The cation radical (19) [λ_{max} 716, 638, and 582 nm, $a_{\text{H}}(1)$ 6.4 mT] was obtained by dissolving 9-benzhydryl-10-phenylanthracene in conc. sulphuric acid or antimony pentachloride-methylene chloride, in which deprotonation from the cation radical should be suppressed.

Similar behaviour was observed in the reaction of the peroxide (21). When (21) was dissolved in sulphur dioxide, a u.v. absorption at 542 nm and an e.s.r. signal (a strong, but broad signal with a total width of 16 mT), which may be attributable to the neutral radical (22), was observed. An absorption at 680 nm, attributable to the methylium ion (23) ($\log \epsilon$ 4.16), then appeared, its intensity increasing during 1 h. The yield of (23) was ca. 20%.

Upon mixing the dihydroepidioxyanthracene (24) with sulphur dioxide, weak u.v. (λ_{max} 710, 660, 590, and 505 nm) (the same spectrum was obtained by dissolving 9-hydroxymethyl-10-phenylanthracene in conc. sulphuric acid) and e.s.r. (poorly resolved spectrum with a total width of ca. 17 mT) spectra were obtained, which may be attributed to the cation radical (25). After 30 min the intensity of the absorption decreased slowly (half initial intensity after 24 h). From the reaction mixture 9-formyl-10-phenylanthracene (26), which may be derived from (25), was isolated in low yield.

A solution of the peroxide (27) in sulphur dioxide showed u.v. absorptions at 670, 640, 585, and 538 nm

and an e.s.r. signal consisting of a broad singlet with a total width of 18 mT. The absorptions disappeared in 6 h. After 48 h 9,10-diphenylanthracene (32) was isolated in 45% yield. The mechanism in Scheme 3 could explain the formation (32) from (27). The cation radical (28) is formed in the first step, from which phenyl migration and subsequent loss of a proton occur to give the intermediate (30) (path c). The intermediate (30) may also be obtained by elimination of SO_4^- from (29), which may be formed from (27) by simultaneous C-O bond cleavage, phenyl migration, and proton loss (path d). The intermediate (30) would be oxidized by sulphur dioxide to the corresponding cation (31), which would then eject a proton and carbon monoxide giving (32). Similar behaviour was observed in the reaction of compound (39). A solution of (39) in sulphur dioxide showed u.v. absorptions at 623, 572, and 520 nm, and an e.s.r. signal consisting of 5 lines [$a_{\text{H}}(4)$ 3.8 mT]. The intensity of the absorptions decreased after 20 min (half initial intensity after 24 h). From the reaction mixture (32) was isolated in 11% yield.



Reaction of 9,10-Dihydro-9,10-epidioxyanthracene Derivatives with Antimony Pentachloride or Conc. Sulphuric Acid.—The reaction of anthracene peroxides with Brønsted acids in the presence of nucleophiles has been extensively studied;¹⁸⁻²⁰ products derived from heterolytic fission of C-O or O-O bonds are obtained. We have examined the reactions of anthracene peroxides with antimony pentachloride or conc. sulphuric acid;

¹⁸ C. Pinazzi, *Ann. Chim. (Italy)*, 1962, **7**, 433.

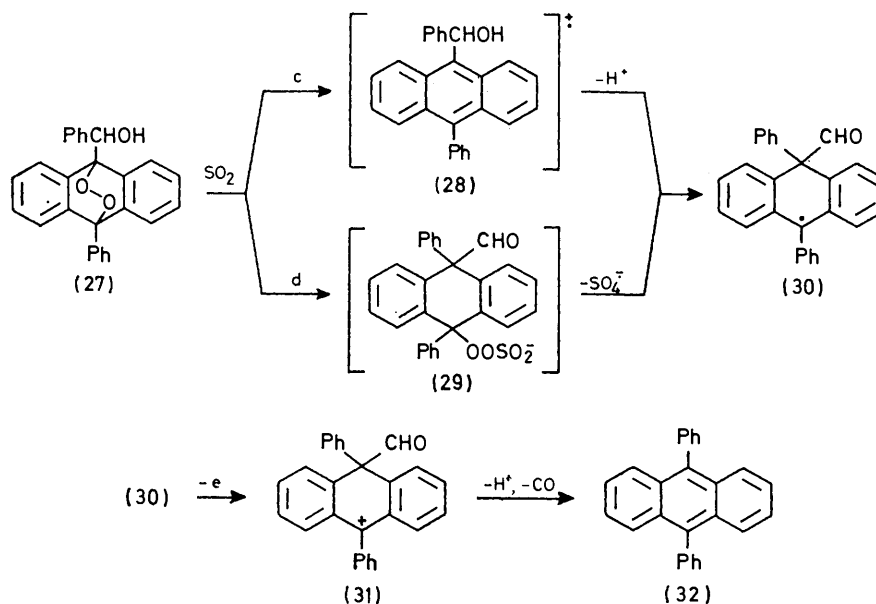
¹⁹ P. F. Southern and W. A. Waters, *J. Chem. Soc.*, 1960, 4340.

²⁰ J. Rigaudy and C. Breliere, *Bull. Soc. chim. France*, 1972, 1390.

we expected the reaction pathways and products would be different in the absence of nucleophile.

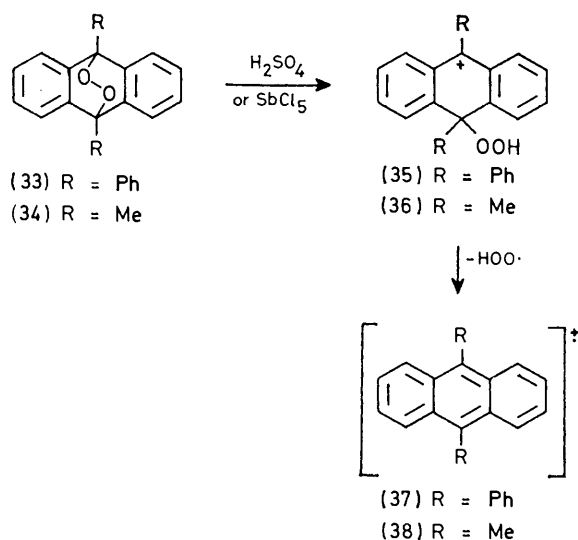
When compound (33) was dissolved in conc. sulphuric acid, u.v. and e.s.r. spectra of the cation radical (37) were obtained immediately and the concentration of (37) (20%, measured by the absorption at 717 nm) did

reaction of compound (34) [15% yield of (38), measured by the absorption at 685 nm]. The cation radicals (37) and (38) could be obtained in yields of 18 and 13%, respectively, by dissolving (33) and (34) in a solution of antimony pentachloride in methylene chloride. These results suggest that the acid-catalysed formation of



SCHEME 3

not change during the reaction. Since (32) is oxidized slowly by conc. sulphuric acid and the concentration of (37) becomes a maximum after 6 h, the possibility that

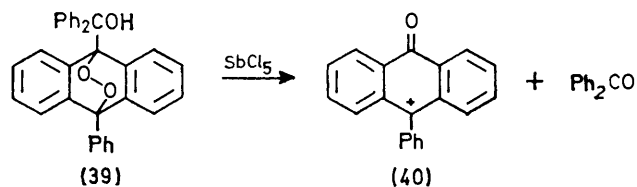


diphenylanthracene first formed from (33) is oxidized by sulphuric acid to afford the cation radical (37) may be discounted. Probably heterolytic C-O bond fission occurs first to give the intermediate (33), from which elimination of the hydroperoxyl radical takes place giving (37). Similar behaviour was observed in the

anthracene cation radicals from the corresponding peroxides is fairly general in the absence of nucleophile.

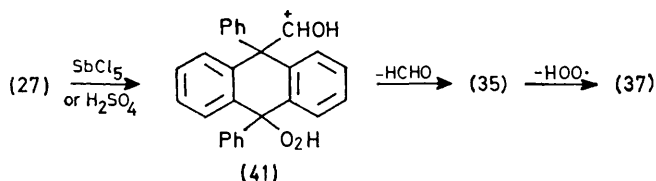
When (39) was dissolved in antimony pentachloride-methylene chloride solution, the carbonium ion (40) was formed immediately and almost quantitatively. From the reaction mixture 10-phenyl-10-hydroxyanthrone and benzophenone were isolated in good yield. The reactions of (18), (21), and (24) with antimony pentachloride afforded the anthrone (44). Similar behaviour was observed in the reactions of these peroxides with conc. sulphuric acid, (44) and polymeric products derived from (44) being isolated from the reaction mixture. These results suggest that selective O-O bond fission with the ejection of, *e.g.*, the hydroxydiphenylmethyl cation takes place in these reactions (Table 2).

In conclusion, heterolytic O-O bond fission occurs selectively when the groups ejected are stable methylum ions, whereas heterolytic C-O bond fission also takes place if the substituents are not good leaving groups.

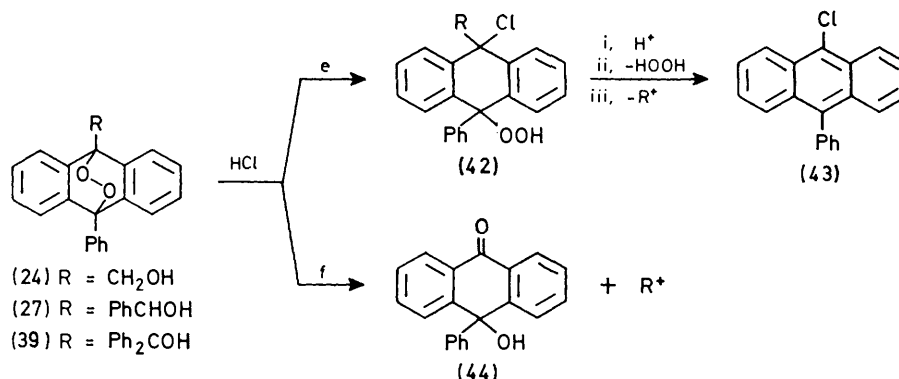


Compound (27) showed different behaviour. Upon dissolution of (27) in sulphuric acid, the formation of

diphenylanthracene cation radical (37) was observed immediately, the concentration of which (45% yield) did not change during the reaction. Similar behaviour was observed in the reaction with antimony pentachloride-methylene chloride. These results strongly



support the existence of phenyl participation which assists the heterolytic cleavage of the C-O bond of (27).



SCHEME 4

The intermediate (41), formed by the above processes, may lose formaldehyde rather than a proton under these strongly acidic conditions giving the intermediate (35).

TABLE 2

Reactions of 9,10-dihydro-9-hydroxymethyl-10-phenyl-9,10-epidioxyanthracene and its derivatives with acid catalysts

Peroxide	Catalyst	Product and % yield
(24)	SbCl ₅	(44) 80
(24)	H ₂ SO ₄	(44) 10 ^a
(24)	HCl	(44) 40, (43) 51
(27)	SbCl ₅	(32) 35 ^b
(27)	H ₂ SO ₄	(32) 43 ^b
(27)	HCl	(44) 50, (43) 41 ^c
(39)	SbCl ₅	(44) 85 ^d
(39)	H ₂ SO ₄	(44) 32 ^{a,d}
(39)	HCl	(44) 60, (43) 31 ^d

^a Polymeric products derived from (44) were also obtained.

^b Benzaldehyde and anthraquinone were obtained as by-products. ^c Benzaldehyde was obtained quantitatively.

^d Benzophenone was obtained quantitatively.

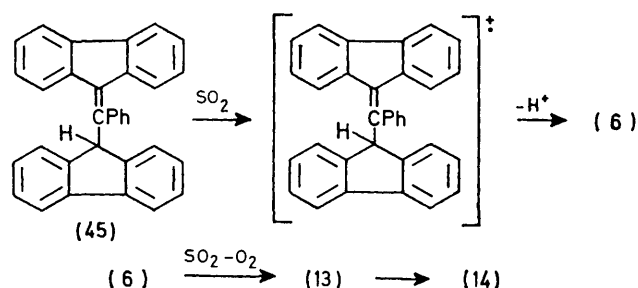
Elimination of the hydroperoxyl radical from (35) is reasonable, as in the reaction of (33).

The reactions of (24), (27), and (39) with hydrogen chloride in ether were also examined. In these reactions chloride ion acts as a nucleophile. From (39) a mixture of 9-chloro-10-phenylanthracene (43) (31%), 10-phenyl-10-hydroxyanthrone (44) (60%), and benzophenone (100%) was obtained. The mechanism in Scheme 4 is

reasonable. The intermediate (42), formed by addition of hydrogen chloride to (39), may be attacked by a proton followed by elimination of hydrogen peroxide and subsequent loss of the hydroxydiphenylmethyl cation to give (39) (path e). In this respect, in the reaction of 9,10-dihydro-9,10-epidioxyanthracene, for example, the addition compound analogous to (42) is stable and isolable.¹⁹ This difference in stability of the addition compound may be explained in terms of the ease with which loss of the hydroxydiphenylmethyl cation takes place. Compound (44) is probably formed by heterolytic O-O bond fission of (39) (path f). Similar results were obtained in the reactions of (24) and (27) (Table 2).

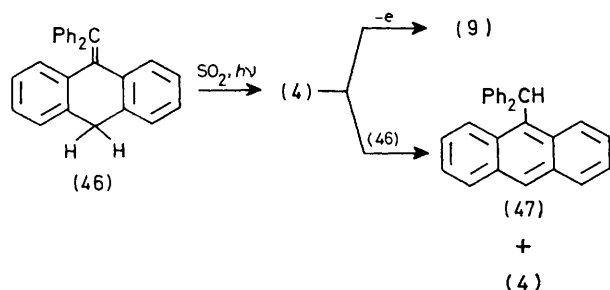
Reactions of Alkenes with Sulphur Dioxide.—When compound (45) was dissolved in sulphur dioxide in the

dark in the absence of oxygen, u.v. and e.s.r. spectra attributable to the fluorenyl radical (6) were observed. The intensity of the absorption increased during the reaction. When the reaction was performed in the presence of oxygen, the radical concentration first increased, and then started to decrease after 12 h. From the reaction mixture the spiro-compound (14) was isolated in 34% yield. The radical (6) may be formed from the cation radical of (45) by proton loss.



Compound (46) reacted only upon irradiation and a weak e.s.r. signal attributable to (4) was observed during the reaction. A u.v. absorption due to (9) was also observed, but its concentration reached only 1% even after 48 h. From the reaction mixture 9-benzhydrylanthracene (47) (5%) was isolated, together with starting material. It is uncertain whether (4) is formed

from the cation radical of (46) by proton loss or directly from (46) by hydrogen abstraction by excited sulphur dioxide.²¹ The reaction of (4) with (46) in chloroform also afforded (47), suggesting that abstraction of hydrogen is the predominant reaction of (4) in the presence of excess of (45). However, the radical (4) is



very stable compared with triphenylmethyl, and is not able to abstract hydrogen even from 9,10-dihydroanthracene.²²

EXPERIMENTAL

E.s.r. spectra were obtained with a JEOL LNM 4P100 instrument, u.v. spectra with a Varian Techron 635 spectrometer, ¹H n.m.r. spectra with a JEOL JNM-PS-100 instrument, and mass spectra with a Hitachi RMU-6H spectrometer. Details of the apparatus used for the reactions in liquid sulphur dioxide have been described previously.²³ Light petroleum refers to the fraction of b.p. 60–80 °C unless otherwise noted.

9-Benzyl-10-phenylanthracene,²⁴ 9-hydroxymethyl-10-phenylanthracene,¹⁸ 9-diphenylmethylene-9,10-dihydroanthracene,²⁵ and 9-(α -fluoren-9-ylidenebenzyl)fluorene²⁶ were prepared by reported methods. The preparation of tris(biphenyl-4-yl)methyl chloride,²⁷ tris(*p*-t-butylphenyl)methyl chloride,²⁸ 9-(α -fluoren-9-ylidenebenzyl)fluoren-9-yl chloride,²⁹ and tris(*p*-nitrophenyl)methyl bromide³⁰ has been described.

9-Chloro-10-diphenylmethylene-9,10-dihydroanthracene was prepared from 9-hydroxy-10-diphenylmethylene-9,10-dihydroanthracene³¹ following the method of Bachmann.³² Recrystallization from benzene–light petroleum gave the pure *chloride*, m.p. 205 °C (decomp.) (Found: C, 85.6; H, 4.9; Cl, 9.3. C₂₇H₁₉Cl requires C, 85.6; H, 5.05; Cl, 9.4%), δ 6.04 (1 H, s), λ_{max} 309 (log ϵ 4.05) and 245 nm (4.41). 9-Chloro-9-phenyl-10-diphenylmethylene-9,10-dihydroanthracene was prepared from 9-hydroxy-9-phenyl-10-diphenylmethylene-9,10-dihydroanthracene.³¹ Recrystallization from benzene–light petroleum afforded the pure *chloride*, m.p. 180 °C (decomp.) (Found: C, 87.3; H, 4.9; Cl, 7.6. C₃₃H₂₃Cl requires C, 87.1; H, 5.1; Cl, 7.8%), λ_{max} 290 (log ϵ 3.84), 260 (3.94), and 240 nm (4.08).

²¹ J. R. Nooi, P. C. van der Hoeven, and W. P. Haslinghuis, *Recl. Trav. chim.*, 1972, **91**, 161.

²² H. G. Lewis and E. D. Owen, *Chem. Comm.*, 1966, 216.

²³ T. Nagai, T. Miyazaki, Y. Sonoyama, and N. Tokura, *J. Polymer Sci., Part A-1, Polymer Chem.*, 1968, **6**, 3087.

²⁴ S. Gibson, A. H. Mosnaim, D. C. Nonhebel, and J. A. Russel, *Tetrahedron*, 1969, **25**, 5047.

²⁵ P. L. Julian, W. Cole, and T. F. Wood, *J. Amer. Chem. Soc.*, 1935, **57**, 2508.

²⁶ C. F. Koelsch, *J. Amer. Chem. Soc.*, 1932, **57**, 4744.

²⁷ W. Schlenk, *Annalen*, 1909, **368**, 295.

9-Benzhydryl-10-phenylanthracene was prepared by the reaction of 9-chloro-9-phenyl-10-diphenylmethylene-9,10-dihydroanthracene with sodium borohydride in aq. diglyme.³³ The crude *hydrocarbon* was purified by column chromatography (\times 2) on basic alumina (elution with light petroleum) and recrystallization from benzene–light petroleum, but did not show a sharp m.p. (Found: C, 94.3; H, 5.75. C₃₃H₂₄ requires C, 94.25; H, 5.75%), *m/e* 420, λ_{max} 398 (log ϵ 3.67), 378 (3.68), 358 (3.46), and 343 nm (3.09). 9-(α -Hydroxybenzyl)-10-phenylanthracene was prepared by reduction of 9-benzoyl-10-phenylanthracene²⁴ with lithium aluminium hydride in ether. Recrystallization from ether gave the pure *hydroxy-compound*, m.p. 190–191.5 °C (Found: C, 89.7; H, 5.6. C₂₇H₂₀O requires C, 90.0; H, 5.5%), *m/e* 360, δ 2.72 (1 H, s), ν_{max} 3 580, 1 045, and 1 030 cm⁻¹, λ_{max} 395 (log ϵ 3.93), 375 (3.96), 355 (3.83), and 338 nm (3.51).

Preparation of 9-(Hydroxydiphenylmethyl)-10-phenylanthracene.—To a solution of 9-phenyl-10-anthryl-lithium, prepared from 9-bromo-10-phenylanthracene (2.2 g) and *n*-butyl-lithium³⁴ in benzene–ether (ether was evaporated off at 80 °C before the following operation), was added a benzophenone (2.0 g) in benzene during 30 min. The mixture was heated under reflux for 1.5 h, while nitrogen was bubbled through. The mixture was poured into ice-cold aqueous ammonium chloride, and extracted (\times 3) with ether. The combined extracts were dried (Na₂SO₄) and evaporated. The pure *alcohol* (1.3 g, 50%) was obtained by column chromatography first on alumina and then on silica gel, followed by recrystallization from aq. ethanol, m.p. 118–122 °C, *m/e* 436, ν_{max} 3 575 and 1 035 cm⁻¹, λ_{max} 401 (log ϵ 3.90), 381 (3.94), 361 (3.76), 345 (3.45), and 268 nm (4.04).

Preparation of Free Radicals.—Radicals were prepared by the reactions of the corresponding chlorides or bromide with silver in benzene or chloroform. The radicals (1)–(4) were prepared *in vacuo*.³⁵ The radicals (5) and (6) were prepared following the method of Ziegler and Boye.³⁰ After isolation solutions containing the radicals were treated in a dry box filled with nitrogen. To measure the oxidation rate of the radicals (1), (2), and (4), they were prepared directly in sulphur dioxide, and after decantation of the radical solution into an e.s.r. tube, the tube was sealed *in vacuo*.

Preparation of Peroxides.—A solution of the appropriate anthracene derivative (200 mg) and Methylene Blue (20 mg) in chloroform (100 ml) was irradiated with a 300 W tungsten lamp at 0 °C for 1 h. The dye was absorbed on charcoal, and the peroxide was isolated by removal of solvent under reduced pressure at room temperature. Addition of ether–light petroleum gave the pure *peroxides* (18), (21), (24), (27), and (39) as white solids. If necessary they were purified by column chromatography on silica gel. (18); m.p. 197–199 °C (Found: C, 87.5; H, 5.75).

²⁸ C. S. Marvel, J. F. Kaplan, and C. M. Himel, *J. Amer. Chem. Soc.*, 1941, **63**, 1892.

²⁹ C. F. Koelsch, *J. Amer. Chem. Soc.*, 1957, **79**, 4439.

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³⁴ J. L. Chalton and R. Agagnier, *Canad. J. Chem.*, 1973, **51**, 1852.

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$C_{33}H_{24}O_2$ requires C, 87.6; H, 5.3%, m/e 452, δ 5.67 (1 H, s). (21); m.p. 203—204 °C (Found: C, 86.0; H, 5.0). $C_{27}H_{20}O_2$ requires C, 79.9; H, 5.2%, m/e 376, δ 4.17 (2 H, s). (24); m.p. 158—160 °C (Found: C, 79.2; H, 5.0). $C_{21}H_{16}O_3$ requires C, 79.7; H, 5.1%, m/e 316, δ 2.20 (1 H, t) and 4.86 (2 H, d), ν_{max} 3 325 cm^{-1} . (27); m.p. 205 °C (decomp.) (Found: C, 82.4; H, 5.1). $C_{27}H_{20}O_3$ requires C, 82.6; H, 5.1%, δ 2.8 (1 H, d) and 6.04 (1 H, d), ν_{max} 3 500 cm^{-1} . (39); m.p. 154 °C (decomp.) (Found: C, 84.8; H, 5.4). $C_{33}H_{24}O_3$ requires C, 84.6; H, 5.1%, δ 4.2 (1 H, s), ν_{max} 3 620 cm^{-1} .

Reaction of Free Radicals with Sulphur Dioxide.—Sulphur dioxide (20 ml) (dried, distilled, and evacuated at 10^{-5} mmHg) was distilled in the dark at -70 °C, into a high-pressure vessel containing the radical (55 mg), the vessel was allowed to warm to 20 °C, and the reaction was continued for 72 h. Absolute ethanol (10 ml) was then added at -70 °C and the reaction was continued at room temperature for 2 h. After conventional work-up, products were isolated by column chromatography.

From (4) 9-ethoxysulphonyl-10-diphenylmethylene-9,10-dihydroanthracene (10) was isolated in 85% yield, m.p. 200 °C (decomp.) (from ethanol) (Found: C, 76.65; H, 5.3; S, 7.0). $C_{29}H_{24}O_3S$ requires C, 77.0; H, 5.35; S, 7.1%, m/e 344, δ 1.3 (3 H, t), 4.12 (2 H, q), and 5.54 (1 H, s), ν_{max} 1 360, 1 170, 1 005, and 930 cm^{-1} , λ_{max} 295 (log ϵ 3.78) and 244 nm (3.89). Compound (10) was also obtained, quantitatively, by keeping a solution of 9-ethoxy-10-diphenylmethylene-9,10-dihydroanthracene (11) in liquid sulphur dioxide at room temperature for 2 h. Compound (11) was prepared by the reaction of the corresponding chloride and ethanol, m.p. 165—166 °C (from benzene-light petroleum) (Found: C, 89.7; H, 6.1). $C_{29}H_{24}O$ requires C, 89.65; H, 6.2%, δ 1.35 (3 H, t), 3.70 (2 H, q), and 5.17 (1 H, s), λ_{max} 297 (log ϵ 4.02) and 242 nm (4.04).

The reaction of (6) was performed in the presence of oxygen (10 ml) and the product (14) obtained was purified by crystallization from toluene-light petroleum (b.p. 100—120 °C), m.p. 197—199 °C (lit.,³⁶ 197—199 °C), m/e 416. The reaction of (5) afforded 9-ethoxy-9-phenyl-10-diphenylmethylene-9,10-dihydroanthracene (16), m.p. 243.5—244.5 °C (from benzene-light petroleum) (Found: C, 90.2; H, 5.95). $C_{33}H_{28}O$ requires C, 90.2; H, 6.1%, δ 1.34 (3 H, t) and 3.31 (2 H, q), λ_{max} 290 (log ϵ 4.0) and 238 nm (4.1). The reaction of (3) in the presence of oxygen, gave tris-(*p*-nitrophenyl)methanol (17) which was purified by recrystallization from acetic acid, m.p. 188—191 °C (lit.,³⁷ 190—191 °C).

Reaction of Peroxides with Sulphur Dioxide.—U.v. and e.s.r. spectra were measured as described previously.⁸ A solution of (18) (200 mg) in degassed sulphur dioxide was kept at room temperature in the dark for 24 h, oxygen (10 ml) was then added, and the reaction was continued for 1 h. Ethanol (10 ml) was then added at -70 °C, and the mixture was kept at room temperature for a further 2 h. After conventional work-up the products were separated by column chromatography on silica gel. Elution with benzene afforded (16) in 34% yield. The reaction of (21) was performed in the absence of oxygen. The products were chromatographed on a silica gel column. Elution with benzene gave 9- α -ethoxybenzyl-10-phenylanthracene

(5%), m.p. 154—156 °C (from ether-light petroleum) (Found: C, 89.5; H, 6.0). $C_{29}H_{24}O$ requires C, 89.65; H, 6.2%, δ 1.22 (3 H, t) and 3.25—3.80 (2 H, m), λ_{max} 395 (log ϵ 3.95), 375 (3.96), 356 (3.83), and 338 nm (3.51), ν_{max} 1 080 cm^{-1} . Elution with ether afforded product (47), which could not be identified, m.p. 205—210 °C (from benzene-light petroleum) (Found: C, 88.4; H, 5.00). $C_{40}H_{26}O_2$ would require C, 89.65; H, 4.8%, m/e 538 and 269, δ 6.8—7.6 (18 H, m), 7.70—7.83 (4 H, m), and 8.20—8.40 (4 H, m), λ_{max} 296 and 270 nm, ν_{max} 1 670, 1 325, 1 285, 935, 815, 755, and 750 cm^{-1} .

The reaction of (23) (200 mg, 0.63 mmol) in sulphur dioxide (20 ml) was performed in the dark in the absence of oxygen for 72 h. After conventional work-up the products were separated by column chromatography on silica gel. Elution with benzene gave 9-formyl-10-phenylanthracene (8 mg, 4%), m.p. 169—171 °C (lit.,³⁸ 167 °C). Elution with ether afforded (47) (130 mg). Reactions of (27) or (39) were performed under the same conditions. From (27) diphenylanthracene (46%), anthraquinone (40%), and benzaldehyde (20%) were obtained. The reaction of (32) afforded diphenylanthracene (11%) and benzophenone (70%).

Reaction of Peroxides with Sulphuric Acid.—To conc. sulphuric acid (50 ml) was added a solution of the peroxide (200 mg) in methylene chloride (50 ml) at room temperature during 10 min. After 5 h the mixture was poured into ice-water and extracted with ether. The peroxide (24) gave a mixture of 10-hydroxy-10-phenylanthrone (44) (10%), m.p. 221—222.5 °C (lit.,³⁹ 215 °C), anthraquinone (50%), and polymeric products. The reaction of (32), gave (44) (32%), anthraquinone (10%), and benzophenone (90%) together with some polymeric products. Solutions in sulphuric acid of (24) or (39) showed the presence of an unidentified radical species derived from (44), λ_{max} 632, 585, 550, and 460 nm, with an e.s.r. signal consisting of more than 30 lines.

From (27) diphenylanthracene (43%), anthraquinone (34%), and benzaldehyde (40%) were obtained.

Reaction of Peroxides with Antimony Pentachloride.—To a solution of antimony pentachloride (2 g) in methylene chloride (50 ml) was added a solution of the peroxide (200 mg) in methylene chloride (50 ml) during 10 min, and the mixture was kept at room temperature for 2 h. The mixture was poured into ice-cold aqueous potassium hydroxide, and extracted with ether. From (24), (44) (80%) and anthraquinone (15%) were isolated. In the reaction of (39) a mixture of (44) (85%), anthraquinone (10%), and benzophenone (90%) was obtained. Solutions of (39) or (24) in antimony pentachloride-methylene chloride showed the formation of the carbonium ion (40) in high yield. The same carbonium ion (40) was obtained by dissolving 9-hydroxy-9-phenylanthrone (44) in antimony pentachloride-methylene chloride, λ_{max} 520 (log ϵ 3.94) and 463 nm (3.96). The reaction of (27) gave a mixture of diphenylanthracene (40%), anthraquinone (30%), and benzaldehyde (10%).

Reaction of Peroxides with Hydrogen Chloride.—Dry hydrogen chloride was bubbled through a solution of the peroxides (24), (27), or (39) (200 mg) in ether (100 ml) at room temperature for 1 h. Compound (44) and 9-chloro-

³⁶ C. F. Koelsch, *J. Amer. Chem. Soc.*, 1932, **57**, 4744.

³⁷ M. F. Hawthorne and G. S. Hammond, *J. Amer. Chem. Soc.*, 1955, **77**, 2549.

³⁸ R. O. C. Norman and W. A. Waters, *J. Chem. Soc.*, 1958, 167.

³⁹ L. Julian and W. Cole, *J. Amer. Chem. Soc.*, 1935, **57**, 1607.

10-phenylanthracene (43), m.p. 175—176.5 °C (lit.,⁴⁰ 173—174 °C) together with the corresponding aldehyde or ketone were isolated (Table 2).

Reaction of 9-(α -Fluoren-9-ylidenebenzyl)fluorene (45) with Sulphur Dioxide.—A solution of (45) (30 mg) in sulphur dioxide (20 ml) in the presence of oxygen (10 ml) was kept at room temperature for 48 h. Chromatographic separation of the products afforded (14) (11 mg, 34%) together with starting material (13 mg).

Reaction of 9-Diphenylmethylene-9,10-dihydroanthracene

⁴⁰ D. Masnain, D. C. Nonhebel, and J. A. Russel, *Tetrahedron*, 1969, **25**, 3485.

(46) with Sulphur Dioxide.—A solution of (46) (50 mg) in sulphur dioxide (20 ml) in a Pyrex tube was irradiated with a Halos PIH 300W high-pressure lamp at 0 °C for 24 h. Chromatography with light petroleum as eluent gave 9-benzhydrylanthracene (47) (2.5 mg, 5%), m.p. 205.5—208 °C (lit.,⁴¹ 204—205 °C), λ_{max} 390 (log ϵ 4.04), 370 (4.05), 352 (3.85), 335 (3.52), 320 (3.11), and 257 nm (5.04). Further elution gave starting material (40 mg).

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