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REACTION OF SUPEROXIDE AND OZONATE RADICAL-IONS WITH 9,10-DICHLORO-9,10-DIPHENYLDIHYDROANTHRACENE

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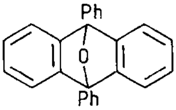
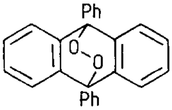
Reaction of (a) superoxide and (b) ozonate radical-ions with the title dichloride does not give the corresponding endo-peroxide and ozonide, respectively. A variety of products formed by nucleophilic substitution and reductive dehalogenation were isolated.

In continuation[1] of our work on the comparative chemistry of superoxide ($O_2^{\overline{\cdot}}$) and ozonate ($O_3^{\overline{\cdot}}$) radical-anions we have examined the reactions of both with 1,2- and 1,4-dihalides. Herein, we describe reactions with 9,10-dichloro-9,10-diphenyl-9,10-dihydroanthracene (8).

Likely products from such reactions are the endo-peroxide (2) (from $O_2^{\overline{\cdot}}$), the endo-oxide (1) and ozonide (3) (from $O_3^{\overline{\cdot}}$). Two of these (1 and 2) are known[2,3] and an analogue of the third has been isolated.[4] In an attempt to prepare the ozonide (3) by conventional means a methylene chloride solution of 9,10-diphenylanthracene was added slowly to a saturated one of ozone in Freon-12 at -90°C. The freon and excess of ozone were allowed to evaporate at room temperature and the insoluble solid (m.p. 185-187°C) which separated was collected. It readily liberated iodine from potassium iodide, exploded when heated above 100°C, or scratched, and sometimes even spontaneously at room temperature. I.r. and n.m.r. spectra were uninformative but its mass spectrum showed a weak molecular-ion peak at m/z 378 corresponding to structure (3) and intense fragment ions at m/z 362 (M^+-O) and m/z 330 (M^+-O_3). Further purification was limited by its frangibility but it was shown (tlc) not to be contaminated with the parent hydrocarbon, endo-peroxide (2) or endo-oxide (1). On this basis it is assigned the ozonide structure (3). Its products of decomposition were also consistent with this conclusion. Thus, separation of the complex mixture which resulted on heating the ozonide (3) to >100°C gave small amounts of the following: 1,2-dibenzoylbenzene (6), 10-hydroxy-10-phenylanthrone (5)[5] and a product which showed ν_{max} 3570(sh) and 3480(br) cm^{-1} and only aromatic proton signals in its nmr spectrum. Its mass spectrum was dominated by the base



(1)



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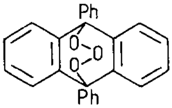

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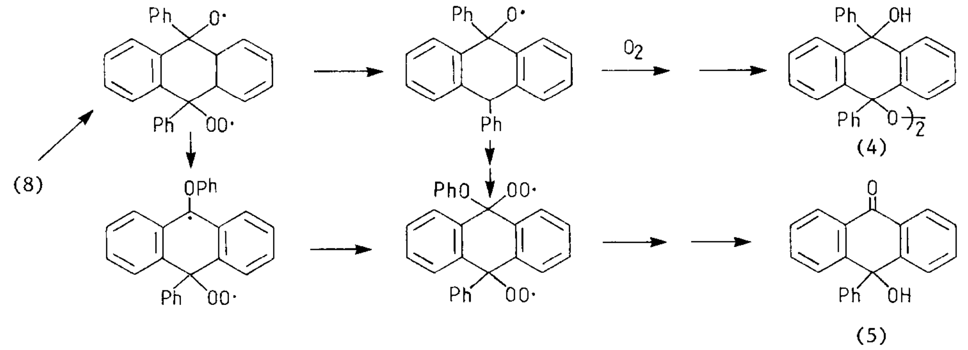
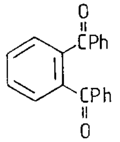
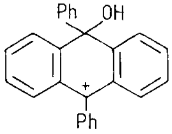


Scheme 1

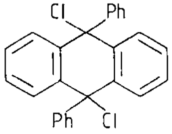
peak at m/z 347 corresponding to the ion (7; $C_{26}H_{19}O$, accurate mass) and an intense peak at m/z 270 ($7^+-C_6H_5$). However, a very weak peak at m/z 363 (7^++O) was also evident. The most likely structure for this product is that of the di-t-alkyl peroxide (4) whose molecular ion (m/z 726) is not detectable but which readily loses molecular oxygen to give the stabilised cation (7) and undergoes O-O homolysis to give the weak $M^+/2$ peak at m/z 363. There is precedent for such losses.[6] Formation of the products (4-5) from the ozonide (3) is not difficult to envisage and could occur via known reactions. One possibility is given in Scheme 1. However, formation of the diketone (6) was surprising and must proceed through a high energy pathway. Speculation on its mode of formation is not justified at this stage.



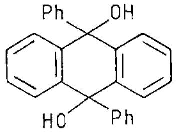
(6)



(7)



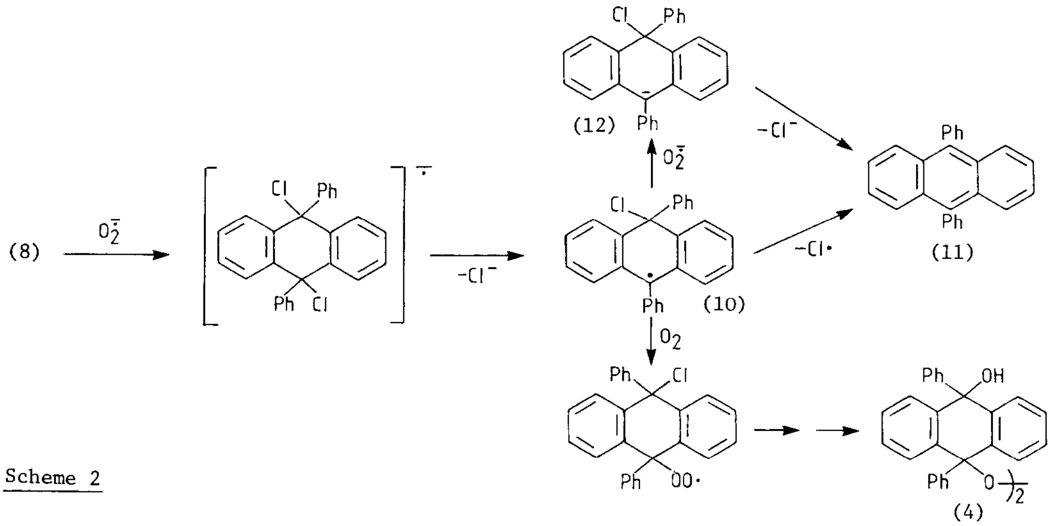
(8)



(9)

Potassium ozonate, prepared as previously described[7] from potassium superoxide in Freon-12, was allowed to react with a solution of the dichloride[8] (8) in methylene chloride for 1 h at -50°C before the Freon was allowed to evaporate and the methylene chloride was removed below room temperature. The mixture of products so-formed did not contain the ozonide (3) nor the endo-oxide (1) but was almost identical (tlc) with that obtained by thermal decomposition of the ozonide except for the presence of 9,10-diphenylanthracene (10%) which with hydroxyanthrone (5) and peroxide (4) were isolated.

Reaction of tetramethylammonium superoxide[9] (1 mol) with the dichloride (8) (1 mol) in benzene-crown ether at room temperature gave none of the endo-peroxide (2) which in a separate experiment was shown to survive such conditions. Instead, much (40%) starting material was recovered and the products, peroxide (4), anthranol (9)[10] and 9,10-diphenylanthracene were isolated. Formation of the anthranol (9) implies that intermolecular nucleophilic substitution by superoxide has occurred at both the 9- and 10-positions.[11] Dehalogenation leading to the parent hydrocarbon implies that electron transfer occurs from superoxide to the dihalide (8) followed by halide loss. However, for simple halides at least this is thermodynamically disallowed[12] (E ≃-1.4 V vs SCE). The corresponding process for the dichloride (8) should be more favourable but confirmatory one electron reduction values are scarce. The most relevant values available are those derived from cyclic voltametry measurements[13] which show a one-electron reduction wave at -0.9 V (vs SCE). Electron transfer as indicated in Scheme 2 would readily account for formation of both the hydrocarbon



Scheme 2

(11) and the peroxide (4) [via (10) → (11) or (10) → (12) → (11)]. The feasibility of electron transfer to other suitably substituted dihalides resulting in overall dehalogenation is under further investigation.

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