Oxygenation Reactions of Diperoxychromium(VI) Oxide Etherate (CrO_5–OEt_2). Possible Role of Singlet Oxygen in the Isolation of 1,2,3,4-Tetraphenyl-5,6-dioxabicyclo[2,2,1]hept-2-en-7-one (Tetracyclone Endoperoxide)

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Summary The title epidioxy-ketone was isolated using diperoxychromium(VI) oxide etherate as an oxygenating reagent in a reaction which may involve singlet oxygen as an intermediate.

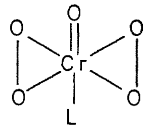
ACID solutions of chromates react with hydrogen peroxide in the presence of organic compounds having a lone pair of electrons (ethers, amines, *etc.*) to yield dark blue solutions of complexes of diperoxychromium(VI) oxide having the general structure (I). Diperoxychromium(VI) oxide etherate (I; L = Et_2O) decomposes at room temperature in a unimolecular reaction to yield oxygen and a mixture of chromium salts.[1] Its solubility in an organic solvent and the precipitation of the otherwise reactive chromium salts during the reaction makes diperoxychromium(VI) oxide etherate an attractive possibility as a mild oxygenating reagent in organic chemistry. In the search for an agent that will promote such reactions under conditions comparable to those of enzyme-catalysed oxygenations some of which are closely related to the reactions of singlet oxygen, the reactions of (I; L = Et_2O) with unsaturated organic compounds are being studied.

When tetraphenylcyclopentadienone is added to a solution of diperoxychromium(VI) oxide etherate and stirred in the dark, at room temperature and under nitrogen for 12 h, the epidioxy-ketone (II),† 1,2,3,4-tetraphenyl-5,6-dioxabicyclo[2,2,1]hept-2-en-7-one, is isolated, in essentially quantitative yield, m.p. 39—41°. It readily liberates iodine from a solution of potassium iodide in aqueous acetic acid. The i.r. carbonyl frequency of the product (1792 cm^{-1} in carbon tetrachloride) and its u.v. absorption [λ_{max} (CH_2Cl_2) 261; ϵ_{max} 21,000] are consistent with its formulation as an analogue of norborn-2-en-7-one.[2] Its mass spectrum has, besides the molecular ion (*m/e* 416), the following peaks: 388, 372, 311, 178, 105, and 77.

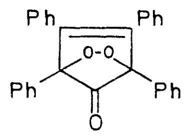
The epidioxy-ketone (II) is stable at low temperatures (*e.g.* it can be kept without appreciable change at −5°) but is readily decomposed in the presence of traces of acid or base. The isolation of (II), apparently the first compound having an αα′-epidioxy-ketone linkage, is therefore a consequence of the mild conditions of its synthesis. At elevated temperatures, it undergoes expected thermal transformations. When a chromatographically homogeneous sample is heated under reflux in benzene solution for 48 h, *cis*-dibenzoylstilbene can be isolated by chromatography in 2% yield [m.p. 216—217°, (lit. 216—217°); i.r. spectrum identical with published data[3]]. The remaining material was isolated as the unchanged epidioxy-ketone (II) and yielded more *cis*-dibenzoylstilbene when subjected to the same conditions. The conversion of (II) into *cis*-dibenzoylstilbene is analogous to the known decarbonylation of norborn-2-en-7-ones.[4] The reaction cannot be brought about more effectively by raising the temperature as other processes then intervene. Pyrolysis at 210° under nitrogen afforded a mixture of products from which the diepoxy-ketone (III)† can be isolated [10% yield; m.p. 196—197°, (lit. 192°)[5]; ν_{max} (C=O) 1755; *m/e* 416]. Further confirmation of this assignment of structure was obtained by the synthesis of the diepoxy-ketone (IV)† on treatment of tetraphenylcyclopentadienone with alkaline hydrogen peroxide [m.p. 164—165°; ν_{max} (C=O); 1755; *m/e* 416]. The conversion of the epidioxy-ketone (II) into the diepoxy-ketone (III) is a direct analogue of the conversion of 1,2,3,4-tetraphenyl-5,6-dioxabicyclo[2,2,1]hept-2-ene (tetraphenylcyclopentadiene endoperoxide) into 1,2,3,4-diepoxy-1,2,3,4-tetraphenylcyclopentane.[6]

Dye-sensitized photo-oxygenation of tetraphenylcyclopentadienone gives rise directly to *cis*-dibenzoylstilbene in high yield. By analogy with similar processes, the mode of this conversion is regarded as involving the addition of molecular oxygen in the $^1\Delta_g$ state to the dienone to form the epidioxy-ketone (II) which undergoes spontaneous loss of carbon monoxide to yield the product.[7] Under conditions where tetraphenylcyclopentadienone is converted into *cis*-dibenzoylstilbene in Methylene Blue-sensitized photo-oxygenation, the epidioxy-ketone (II) was unaffected. The intermediacy of (II) in that reaction can, therefore, be seriously questioned. In particular, the possibility that the reaction of tetraphenylcyclopentadienone, unlike other dye-sensitized photo-oxygenations, involves an excited triplet state of the dienone and ground-state oxygen cannot, at present, be excluded.

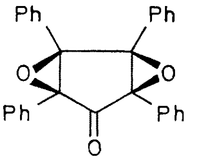
The decomposition of diperoxychromium(VI) oxide etherate to give singlet oxygen together with initial products of chromium also having singlet multiplicities is a process allowed by spin-conservation. The formation of the epidioxy-ketone (II) from the reaction with diperoxychromium(VI) oxide etherate may therefore involve the decomposition of the latter to yield singlet oxygen as an initial process. This is further indicated by the conversion of 1,3-diphenylisobenzofuran into 1,2-dibenzoylbenzene on treatment with diperoxychromium(VI) oxide etherate—a process which is much more efficient than the formation of (II) from tetraphenylcyclopentadienone. This is in agreement with the fact that 1,3-diphenylisobenzofuran is the most reactive known substrate of singlet oxygen.[8] However, preliminary studies on the decomposition of diperoxychromium(VI) oxide etherate in the presence of the dienes do not rule out the possibility of a bimolecular reaction between them. The kinetics of this system are complex due, at least in part, to the possible existence[1] of more than one pathway for the decomposition of diperoxychromium(VI) oxide etherate.



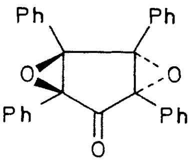
(I)



(II)



(III)



(IV)

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† Satisfactory elemental analyses were obtained for these compounds, which have no ^{1}H n.m.r. absorption above τ 3·3.

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