The following general procedure is representative for the transformation of **2a** or **2b** to the substituted cis diols **1**. To a cooled (−40°) solution of 3.3 mmol of lithium diethylamide (from butyllithium and diethylamine) in 10 ml of dry THF under nitrogen is added 1–1.5 ml of dry hexamethylphosphoramide followed by 1.5 mmol of **2a** or **2b** in 4 ml of THF with stirring. The deep red solution of anion **7** is stirred for 30 min at which time the alkyl halide, R–X (1.6 mmol), is added either as a neat liquid or in a minimum volume of THF. Stirring is continued for an additional 30 min at −40° and 2 ml of a 50% aqueous solution of diethylamine is added to the reaction. The cold bath is removed and the reaction mixture is allowed to warm to room temperature and stirred ~2 hr to effect rearrangement and cleavage of **8** to the cis diol **1**. The cis diols **1** listed in Table I are purified by chromatography on neutral alumina (activity III).[5,7] The cis-diol stereochemistry is readily assigned by examination of the ^{1}H nmr chemical shifts and splitting patterns of the C-4 methylene protons.[14]

This approach to substituted, dioxygenated cyclopentenes differs from the alternate synthesis of such derivatives obtained *via* singlet oxidation of alkylcyclopentadienes[15] in one significant aspect. The inherent design of this reaction sequence affords the possibility of obtaining chiral cyclopentenediols **1** from precursors that may be chemically resolved. We are presently engaged in executing this idea and are developing methods for the elaboration of **1** to optically active prostanoids in the E and F series.

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Singlet Oxygen Oxidation of Phosphites to Phosphates[1]

Summary: Singlet oxygen is shown (by means of Stern–Volmer analysis using β-carotene) to oxidize trialkyl phosphites to trialkyl phosphates in quantitative yield; relative rates of reaction are given for several phosphites.

Sir: We wish to report the dye-sensitized photooxidation of several trialkyl phosphites and the compelling evidence that the active oxidizing agent is singlet molecular oxygen.

Several trialkyl phosphites were irradiated with visible light[2] in acetone solution in the presence of Rose Bengal (RB)[3] while oxygen was bubbled through the solution continuously. In each case, the phosphate was formed in good yield as the only detectable product; the results are summarized in Table I. No reaction occurred in the dark or in the absence of dye.

Table I

Compound	Yield,[a] %	k_{rel}[b]	k_1, l. mol^{-1} sec^{-1}[c]
$(MeO)_3P$	85.4	0.65	1.52×10^7
$(EtO)_3P$	87.9	1.00	2.45×10^7
$(i\text{-PrO})_3P$	66.2		
$(n\text{-BuO})_3P$	82.4	0.78	
$(c\text{-}C_6H_{11}O)_3P$	83.0	0.60	
$(CH_2{=\!=}CHCH_2O)_3P$	69.5		

[a] Products isolated by distillation or chromatography and crystallization, and identified by boiling point or melting point and ir comparison to authentic samples. [b] Determined by parallel irradiations using RB in acetone. [c] Determined by means of Stern–Volmer plot, employing MB, β-carotene, and benzene–methanol, 4:1 (v:v).

Although phosphites can be oxidized by ground-state oxygen in a photoinitiated free radical chain process,[4] the dye-sensitized photooxidation was only slightly retarded by

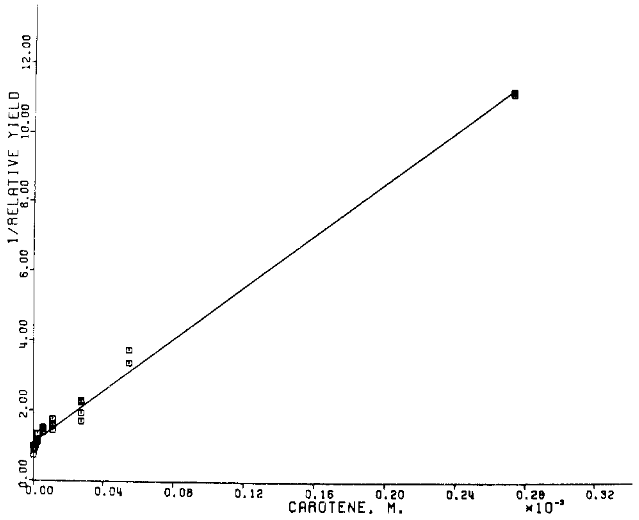

Figure 1. Stern–Volmer plot of β-carotene quenching of the photooxidation of trimethyl phosphite, 0.051 *M* in benzene–methanol (4:1 by volume) using Methylene Blue sensitizer.

the addition of hydroquinone, as expected for a singlet oxygen oxidation.[5] The intermediacy of singlet molecular oxygen in dye-sensitized photooxidations has frequently been inferred from competition between the substrate and known singlet oxygen acceptors, or from the observation of an identical reaction brought about by singlet oxygen formed by nonphotochemical means.[6] Such methods are inapplicable in this case, since phosphites are oxidized by the oxidation products (hydroperoxides and endoperoxides) of the usual singlet oxygen acceptors and also by the reactants (hydrogen peroxide, phosphite ozonides) usually used to prepare singlet oxygen in the dark.[7] Therefore we turned to the specific quenching by energy transfer of singlet oxygen by β-carotene and by 1,4-diazabicyclo[2.2.2]octane (Dabco).[5,6] Phosphate formation was quenched cleanly by both quenchers, and linear Stern–Volmer plots (see Figure 1) were observed in every case attempted. Singlet oxygen is thus confirmed as the oxidizing agent in this reaction.

The most attractive reaction mechanism is shown in Scheme I. The lack of reversibility of step 4 was shown by a linear plot of relative ϕ^{-1} (phosphate) *vs.* [phosphite]$^{-1}$, but the possibility of quenching by phosphite cannot be eliminated. Since k_d for singlet oxygen and the rate constants for β-carotene quenching of singlet oxygen are known for the solvent used, the rates of step 4 can be obtained from the slopes of the Stern–Volmer plots and are included in Table I. These rates are comparable to the rates of reaction of singlet oxygen with tetrasubstituted olefins and correlate with the electron-releasing ability of the alkoxy groups.

Scheme I

			Rate
1.	$^1RB + h\nu$	$\longrightarrow {}^1RB^*$	I_0
2.	$^1RB^*$	$\longrightarrow {}^3RB^*$	k_{isc}
3.	$^3RB^* + {}^3O_2$	$\longrightarrow {}^1RB_0 + {}^1O_2$	k_s
4.	$(RO)_3P + {}^1O_2$	$\longrightarrow (RO)_3P{\cdot}O_2$ (1)	k_1
5.	$1 + (RO)_3P$	$\longrightarrow 2(RO)_3PO$	k_2

The structure of the intermediate 1 cannot be deduced from the information available at this time. An intermediate of the same stoichiometry was proposed for the direct oxidation of phosphites and phosphines by phosphite ozonides,[8,9] and similar intermediates were proposed for the singlet oxygen oxidations of disulfides[10] and sulfides.[11] In the latter case, a zwitterionic structure (R_2S^+–O–O$^-$) was suggested based on solvent effects. A similar intermediate may be expected in the photooxidation of phosphites.

We are continuing to explore the scope of this reaction and seeking evidence for the structure of the intermediate.

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Nonstereospecific Diels–Alder Reactions. I. Reaction of Hexachlorocyclopentadiene with 1,2-Disubstituted Ethylenes

Summary: The Diels–Alder reaction of hexachlorocyclopentadiene and related dienes with a variety of trans-substituted ethylenes takes place with partial to extensive, *de facto* violation of the cis principle, including in one instance the loss of the structural integrity of the dienophile; two concurrent mechanisms, one involving concerted cycloaddition and the other biradical intermediates, are considered for the products.

Sir: The immense success of the Diels–Alder reaction in synthesis is due to a great extent to its stereospecificity whereby the steric integrity of the reactants is preserved in the adducts. This behavior, known as the cis rule, is considered to be the cardinal stereochemical principle of the Diels–Alder reaction.[1] We wish to report now on an extensive series of Diels–Alder reactions of hexachlorocyclopentadiene (1) in which the steric integrity of the dienophile was lost in the adduct, often extensively, in a clear, *de facto* violation of the cis rule.

To develop a rationale for the failure of 1 to form a Diels–Alder dimer on heating,[2] a possible result of steric hindrance between the chlorines of the incipient bridge and the exo positions, we investigated the reaction of 1 with *trans*-1,2-dichloroethylene (2). Heating the pure reactants