First, the dissociation of **2** to singlet oxygen and triphenyl phosphate is not reversible. At −78° no **2** was formed on a 3-hr irradiation of a mixture of triphenyl phosphate, rose bengal, and oxygen in methylene chloride–methanol with a 500-W incandescent lamp. The absence of **2** was established by the sensitive test of warming slowly with 0.20 equiv of rubrene. The rubrene color remained unchanged, and thin layer chromatography showed no transannular peroxide. Under the same conditions **2**, prepared from triphenyl phosphite and ozone, reacted completely with rubrene on warming.

Second, competitive reactions in methylene chloride at −78° between tetramethylethylene and 2,5-dimethylfuran (**6**) show that the former is far more reactive toward **2**, but the latter is much the stronger competitor under conditions of photosensitization where the evidence strongly favors free singlet oxygen as the reagent.[3,6–8] At −78° methylene blue photooxidation (lower curve of Figure 2) shows a ratio k_4/k_6 of 0.090 ± 0.017,[9] whereas in thermal reaction with **2**, k_4/k_6 is of the order of 10 (upper curve of Figure 2).

Sensitized oxidation of **6** alone gave a solution with a simple nmr spectrum consistent with the 2,5-endoperoxide (singlets at δ 1.7 and 6.3). Triphenylphosphine yielded 3-hexene-2,5-dione, isolated as its bis-2,4-dinitrophenylhydrazone, mp 287.5–289° (lit.[10] 289.0–289.5°), in 61% yield. The nmr spectrum of the reaction product from **2** and **6** showed more complex, unresolved signals indicative of a mixture of products, and the bis-DNP was isolated in only 25% yield.

The fact that radical-initiated autoxidation of tetramethylethylene gives exclusively[11] the hydroperoxide **5**, and not the isomeric 2,3-dimethyl-1-hydroperoxy-2-butene, suggests that **2** might be serving in the present case as a chain initiator. However, the inhibitors diphenylamine and 2,6-di-*t*-butylphenol have no effect on the preference of **2** for attacking **4** rather than **6** (Figure 2). Also a reaction between **2** and **4** carried out in the presence of dissolved oxygen gave no greater amount of hydroperoxide than a reaction purged of oxygen by a stream of nitrogen. Thus triphenyl phosphite ozonide donates O_2 at low temperatures by a mechanism which neither involves a chain reaction nor starts one incidentally.

Direct peroxidation by way of free singlet oxygen, though now a widely accepted mechanism for photooxidation, is a relatively recent one. Donation of O_2 by way of a peroxy radical[12] or biradical[13] was proposed many years ago and has not been excluded in any completely general way.

Our present evidence indicates that there is a mechanism of direct O_2 donation from triphenyl phosphite ozonide which yields the same products as free singlet oxygen but has very different selectivities toward different substrates. The Ziegler and Schenck mechanisms both involve the concept of activation of oxygen by the formation of a peroxy radical with an exceptionally weak C–O bond; it has been demonstrated that triphenylmethylperoxy[12] is such a radical.[14] However, unlike the present case, Ziegler's autoxidation catalyzed by the triphenylmethyl radical was a chain reaction with very long chains.[12] Consideration is being given to the possibility of a bimolecular simultaneous donation of two oxygen atoms by **2**; however, any mechanism must take account of the dissymmetry indicated by the fact that the hydroperoxide-forming reactions of singlet oxygen are imitated by the direct process so much more effectively than is the conjugate 1,4 addition.

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Triplet Yield Determinations at High Concentrations of *cis*-Piperylene

Sir:

Piperylene has been commonly used in triplet counting experiments.[1,2] Usually a concentration of ~0.1 *M* is sufficient to quench available photoexcited triplets and to determine the triplet yield of an organic molecule. In the course of investigating the triplet yields of molecules as a function of piperylene concentration, it was observed that the isomerization quantum yield increased unexpectedly at high concentrations of piperylene (>1.0 *M*). In order to remove any uncertainties that may arise from the molecular system under study we have reinvestigated the triplet yield of benzophenone determined from the sensitized *cis–trans* isomerization of *cis*-piperylene. The concentration of *cis*-piperylene was varied over the range 0.08–10 *M* and all photolyses were performed at 366 nm. Benzophenone has been commonly used as a standard with a triplet yield of unity.[1] The analysis of our data for concentrations of <1.0 *M* piperylene was satisfactorily described by the following equation[3]

$$1/\Phi' = (1/\phi_{\mathrm{T}})[1 + k_{\mathrm{dt}}/k_{\mathrm{et}}(cis\text{-P})] \qquad (1)$$

where Φ' is the isomerization quantum yield or apparent triplet yield, defined as $\Phi_{c\rightarrow t}/f$, $\Phi_{c\rightarrow t}$ is the experimentally measured *cis–trans* isomerization yield, $f = 0.55$ is the fraction of triplets which decays to *trans*-piperylene,[1] ϕ_{T} is the triplet yield of the sensitizer, k_{dt} is the rate constant for deactivation of the sensitizer triplet, and k_{et} is the rate constant for triplet–triplet energy transfer between sensitizer and piperylene. When the concentration of *cis*-piperylene was >1.0 *M*, however, the isomerization yield, Φ', increased to values larger than unity. This result suggests that some new process may be occurring. It has been reported that there is no concentration effect on the triplet yield of benzophenone in the concentration range 0.005–0.2 *M* *cis*-piperylene.[1]

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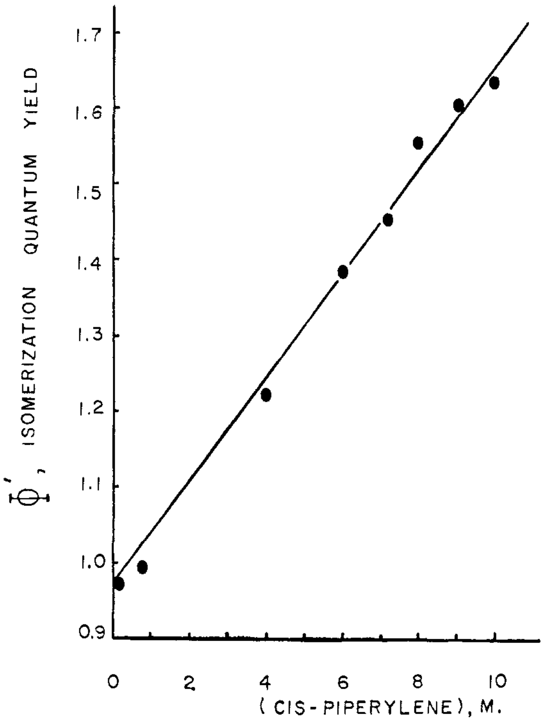

Figure 1. Benzophenone-sensitized *cis–trans* isomerization quantum yields as a function of *cis*-piperylene concentration: concentration of benzophenone, 2 × 10^{-2} *M*; 366-nm excitation.

In view of the isomerization yields exceeding unity in the case of benzophenone, the interaction of the piperylene triplet with its ground state is an inviting possibility. The following two reactions could lead to isomerization efficiencies greater than unity

$$P^{*3} + cis\text{-P} \longrightarrow trans\text{-P} + P^{*3} \qquad (2)$$

$$P^{*3} + cis\text{-P} \longrightarrow \begin{bmatrix}\text{diradical addition}\\ \text{to ground state}\end{bmatrix} \rightsquigarrow \alpha\, cis\text{-P} + (2 - \alpha)trans\text{-P} \qquad (3)$$
$$(\alpha < 1)$$

where P^{*3} is the piperylene triplet that decays to either *cis* or *trans* isomer. The overall effect in reaction 2 is to isomerize a *cis* molecule, while still maintaining a triplet piperylene for isomerization. In reaction 3, diradical addition to the ground state followed by fragmentation may lead to a predominance of *trans* molecules in their ground state. Both reactions result in isomerization enhancement involving a triplet state and a ground state molecule of piperylene. The triplet state energies for the *cis* and *trans* isomers have been reported to be: *cis*-piperylene = 57 kcal, *trans*-piperylene = 59 kcal.[1,4] Although piperylene has been shown to quench singlet states of aromatic hydrocarbons,[5] the singlet lifetime of benzophenone ($\leq 10^{-10}$ sec) is probably too short-lived to be quenched; consequently, it would appear that only the benzophenone triplet is involved in the sensitization process. Inclusion of reactions 2 and 3 into the present reaction scheme results in eq 4, where k_x is the combined rate

$$\Phi' = \phi_T[1 + k_x(cis\text{-P})/k_{dt}'] \qquad (4)$$

constant for reaction between the piperylene triplet and *cis*-piperylene in the ground state, and k_{dt}' is the rate constant for deactivation of the piperylene triplet to a *trans*-ground state. This equation predicts a linear relationship between Φ' and (*cis*-P), with an intercept equal to ϕ_T, which is unity for benzophenone. The results of the experiments in this laboratory are plotted in Figure 1 and obey eq 4 satisfactorily. It can be seen that the intercept is indeed unity within experimental error. Determination of the slope from Figure 1 indicates a ratio of 0.064 M^{-1} for k_x/k_{dt}'. It should be noted that the actual sensitized *cis–trans* isomerization yield of *cis*-piperylene has increased from 0.55 to 0.90 in the concentration range studied. Since the lifetime of the piperylene triplet is unknown, it is difficult to determine an accurate value for k_x; however, Hammond, *et al.*,[6] have estimated that diene triplets live at least 5 × 10^{-6} sec and probably longer. Using their value for k_{dt}', the value of k_x is estimated to be $\sim$1.3 × 10^4 M^{-1} sec^{-1}. The low value for k_x is surprisingly close to the value for diradical addition of the isoprene to its ground state to form dimers,[6] and suggests that possibly reaction 3 may be the source for isomerization enhancement.

There is the need for caution in determining the triplet yield of a sensitizer by *cis–trans* isomerization, since disappearance of *cis*-piperylene *via* dimerization could lead to high values of $\Phi_{c\rightarrow t}$ when analysis is determined by vpc of the *cis–trans* ratios.[7] The data of this paper were obtained by the following two methods: (a) *cis–trans* isomerization ratios and (b) direct comparison of *trans* concentration with known solutions. Although method a gave consistently higher results than method b, the agreement was within 10%. It follows, therefore, that dimerization is not a major contribution to the triplet counting experiments.

The above effect does not alter triplet yield determinations reported in the literature, since their determinations are performed at piperylene concentration <1.0 *M*. It is not unexpected, however, that other olefins may show similar enhancement at high concentrations.

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Stabilization of a Thioketocarbene through π-Complex Formation. Synthesis and Structure of *Trihapto*-1,2-diphenylthioketocarbene–Hexacarbonyldiiron

Sir:

Thioketocarbenes are hypothetical 1,3 dipoles,[1] which have been implicated as intermediates in the thermolysis of 1,2,3-benzothiadiazole[2] or the photolysis of 4-phenyl-1,2,3-thiadiazole.[3] 1,2-Diphenylthioketocarbene, $(\dot{C}_6H_5)C(=S)CC_6H_5$ (**2**), has been suggested to occur in the pyrolysis of certain metal dithienes,[4]

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