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PHOTOSENSITIZED OXYGENATION OF DIARYLMETHYLENETRIPHENYLPHOSPHORANES

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Several diarylmethylenephosphoranes themselves, act as triplet sensitizers to give singlet oxygenation products, i.e., benzophenones and triphenylphosphine oxide, efficiently upon photoirradiation.

Key words: phosphorus ylide; diarylmethylenephosphorane; photo-sensitized oxygenation; singlet oxygen.

INTRODUCTION

Oxygenation of a phosphorus ylide (a phosphorane) has recently been applied in many synthetic procedures.^{1–6} For example, oxygenation of phosphoranes with *N*-sulfonyloxaziridine⁶ and phosphite-ozone adduct² as oxidizers are of special significance. In these, focusing on the singlet oxygenation of phosphoranes, examples have been reported for bis(phenylthio)methylene-¹ and methoxycarbonylalkyldienephosphoranes.³ Wasserman *et al.*⁵ applied this procedure for the preparation of unique vicinal tricarbonyl compound. During our study of the reaction of stable diarylmethylenephosphoranes, some ylides of sufficient stability toward oxygen have shown enhanced reactivity to oxygen upon photoirradiation. Although the reaction corresponds to the photooxygenation of a phosphorane reported by Adam *et al.*,¹ mechanistic detail has not yet been fully elucidated. We, therefore, studied the reaction in more detail and herein, we wish to report on our results. The present work is thus complementary to the work of Adam *et al.*

RESULTS AND DISCUSSION

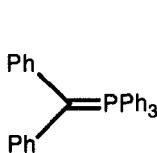
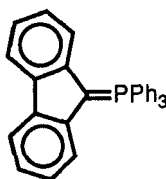
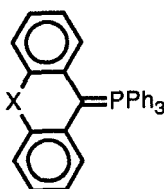
Objective phosphoranes (**1a–f**) were prepared by the usual procedure via their phosphonium salts.^{7–10} Although a benzene solution (6×10^{-3} M) of **1b** was allowed to stand for 5 h with bubbling of oxygen gas at 30–40°C, no formation of oxidized product was detected. In contrast, **1a** could not be handled under usual aerated condition. The stability of **1b** is thus evident. Photo and thermal reactions of **1b** were further studied and the results are shown in Table I. Direct irradiation of **1b** with a Xe lamp in benzene through Pyrex filter gave no product and after a prolonged irradiation, an only intractable tarry material was obtained with a large portion of recovery under inert atmosphere (entries 1 and 2). Introduction of oxygen, to a benzene solution of **1b** gave exclusive products, fluorenone (**3**) and triphenylphosphine oxide (**4**) in almost quantitative yields upon photoirradiation

TABLE I
 Reactions of fluorenylidetriphenylphosphorane (**1b**)^a under various conditions

Entry	Solv.	Temp. (°C)	Time (h)	Atmos- phere	Additive [Conc., M]	Yield (%)		
						Recovery, (1b)	(3)	(4)
1	PhH	RT	10	Ar	---	100	--	--
2	PhH	RT	50	Ar	---	96	--	--
3	PhH	RT	4	O ₂	---	--	86	82
4	MeNO ₂	RT	4	O ₂	---	7	86	83
5	PhH	RT	4	O ₂	DBP ^b [5.7×10 ⁻³]	--	85	84
6	PhH	80	7	Air	KO ₂ [1.3×10 ⁻²] crown ether ^c [4.7×10 ⁻⁴]	95	--	--
7	PhH	RT	4	O ₂	DABCO ^a [5.7×10 ⁻³]	37	60	54
8	PhH	80	48 ^a	Ar	DPAP ^d [3.6×10 ⁻²]	45	49	46

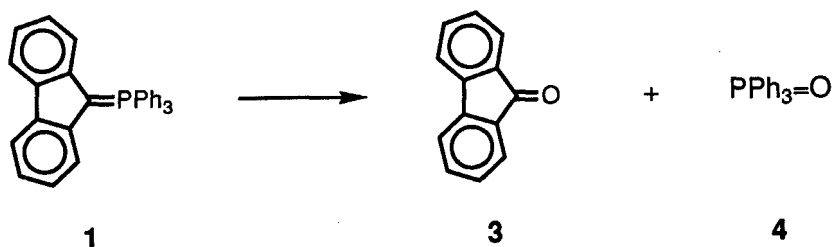
^a[**1b**] = 10⁻² - 10⁻³ M. ^b2,6-Di-*t*-butylphenol. ^cDibenzo-18-crown-6 was employed. ^d1,4-Diazabicyclo[2.2.2]octane. ^eThe reaction time is equal to 3-half lives of DPAP.¹⁰ ^f9,10-Diphenylanthracene-9,10-endoperoxide.

(entry 3). Photoirradiation is essential to the reaction as examined by comparison with a dark control experiment.

**1a****1b****1c**, X = O**1d**, X = S**1e**, X = -CH₂-CH₂-**1f**, X = -CH=CH-

Various processes and intermediates can be considered to account for this oxygenation reaction, i.e., a radical, superoxide, photoexcitation of a ground state charge-transfer complex, an exciplex with oxygen, and singlet oxygenation, etc. In the presence of the known radical scavenger, 2,6-di-*t*-butylphenol (DBP),¹¹ no obvious change in the reaction was observed (entry 5). Entry 6 was intended to estimate the influence of the superoxide anion radical. The reaction failed. It has been of recent interest that photoexcitation of the charge-transfer absorption band formed by an electron-rich organic substance and oxygen leads to various reactions, e.g., nucleophilic substitution via a cation radical, dimerization, and oxygenation, etc.¹² However, no absorption band assignable to a charge-transfer complex between **1b** and oxygen was observed in the UV-VIS spectra. The excited complex (exciplex) has also been widely recognized as an important intermediate for photoreactions.¹³ Characteristic fluorescence emission due to an exciplex formation is observable in some cases. In our case, however, no exciplex fluorescence between

1b and oxygen was observed and also the typical solvent effect due to the exciplex formation¹⁴ was not observed in entry 4 at all.



In comparison with these negative observations, 1,4-diazabicyclo[2.2.2]octane (DABCO)¹⁵ retarded the reaction remarkably as shown in entry 7 and the thermal reaction in the presence of 9,10-diphenylanthracene-9,10-endoperoxide (DPAP) which has been known as the thermal singlet oxygen producing agent,¹⁶ gave rise to the formation of **3** and **4** in almost quantitative yields as shown in entry 8. All these observations support favorably the operation of singlet oxygen in the present case.

If the reaction follows the aforementioned singlet-oxygen path, the singlet oxygenation should occur similarly in the other phosphoranes because of the seemingly higher triplet energy of diarylmethylenephosphoranes. The reactivity, therefore, of **1** was estimated by the time course of the oxygenation reaction as shown in Figure 1. For comparison, the triplet energy of the corresponding benzophenones and the pseudo first order reaction rate of the oxygenation of **1** are listed in Table II. Based on the recent study related to the singlet oxygenation mechanism, the quenching of high-energy triplets by ground-state oxygen does not yield $^1\text{O}_2$ ($^1\Delta_g$) with unit efficiency.¹⁷ Furthermore, the stability of each phosphorane is also different. Thus, the oxygenation reactivity of phosphoranes treated in our experiments seems to be irrelevant to the triplet energies of phosphoranes. As shown

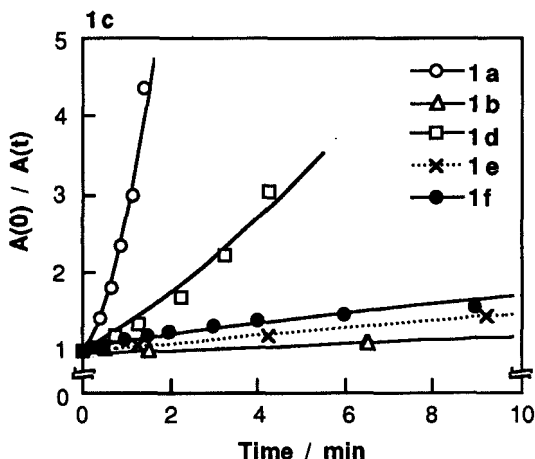


FIGURE 1 Time course of the photooxygenation of diarylmethylenephosphoranes **1**. $[\mathbf{1}] = \text{ca. } 10^{-5}$ M in oxygen-purged cyclohexane. $A(0)$ and $A(t)$: absorbance of **1** at their absorption maxima at time = 0 and t , respectively. Reaction of **1c** was too fast to measure by this method.

TABLE II
Pseudo first order oxygenation reaction rate of phosphoranes (1a-f) and triplet energy of the corresponding benzophenone derivatives

Phosphorane	Rate (s ⁻¹)	benzophenone derivative	E _T (kcal·mol ⁻¹) ^a
1a	1.5×10 ⁻³	benzophenone	68.6
1b	2.9×10 ⁻⁴	fluorenone	53.3 ^b
1c	> 10 ⁻³	xanthone	74.0
1d	4.0×10 ⁻³	thioxanthone	65.5
1e	6.4×10 ⁻⁴	dibenzosuberone	--
1f	1.9×10 ⁻³	dibenzosuberone	--

^a The value denotes the triplet energy of benzophenones measured in non-polar solvents.

in Figure 1 and Table II, however, all phosphoranes are oxidized efficiently upon photoirradiation, albeit there is a rate difference of two order of magnitude. This result suggests additionally the singlet oxygenation of phosphoranes in which the phosphorane itself acts as the triplet sensitizer.

EXPERIMENTAL

Melting points were determined in glass capillaries and were uncorrected. ¹H NMR spectra were recorded on a Hitachi R-24B spectrophotometer at 60 MHz using TMS as an internal standard. UV-VIS spectra were measured with a Hitachi 124 and Shimadzu UV-3000 spectrophotometers. Fluorescence spectra were measured with a Hitachi 650 fluorescence spectrophotometer. Photochemical reactions were performed in a quartz cell using a Wacom Xe lamp KXL-500F (500 W) with a glass filter (Toshiba UV-31, >280 nm) or in a Pyrex test tube using the same lamp. The benzene used was dried over CaH₂. Benzene is a suspect cocarcinogen and usual safety precaution is encouraged.

A General Procedure for Photolysis of Phosphorane 1b. A benzene solution (10⁻³ M) of **1b** in a small Pyrex test tube (φ 15 × 100 mm) was irradiated under Ar or O₂ with a Xe lamp in a temperature controlled water bath. After the irradiation of appropriate reaction time, the solution was concentrated in vacuo and the residue was recrystallized from EtOAc to give **4** as colorless crystals.

The filtrate was further separated by a silica-gel column chromatography (Merck, 230–400 mesh) using 10% EtOAc-hexane as eluent. Benzophenones **3**, the residual **4**, and the recovered **1b** in some cases were obtained.

An Attempted Reaction of Phosphorane 1b in the Presence of Additives. Attempted photolyses (entries 5 and 7) and workup were done in the same manner as described above in the presence of each additive. Thermal reactions (entries 6 and 8) were done in a small reaction vessel (φ 15 × 100 mm) in a temperature controlled oil bath. All recovery and product yields which were calculated after chromatographic separation with sufficient purity or recrystallization, were listed in Table I.

Measurement of the Time Course of the Oxygenation of Phosphoranes 1. Cyclohexane solutions of phosphoranes (2–8.5 × 10⁻³ M) were purged with oxygen for 5 min in an ice bath. After irradiation of the samples at appropriate intervals with a Xe lamp using a glass filter (Toshiba, UV-31), the intensity changes of the absorption maxima of phosphoranes were measured immediately by UV-VIS spectrophotometer. In case of **1c**, the reaction was too fast to measure the time course by this way. Within this range of phosphorane concentration, absorbance of phosphoranes follows strictly Beer's Law.

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