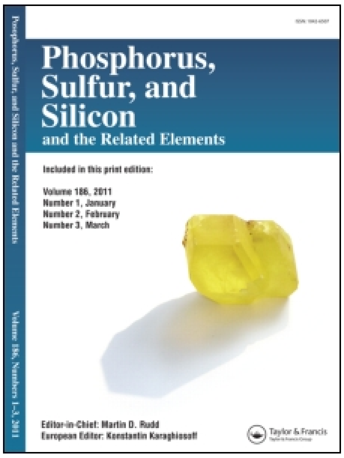

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PHOTOSENSITIZED OXYGENATIONS OF DIMETHYL FLUORENYLIDENETRIBUTYL-AND TRIPHENYLPHOSPHORANYLI-DENESUCCINATE

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PHOTOSENSITIZED OXYGENATIONS OF DIMETHYL FLUORENYLIDENETRIBUTYL- AND TRIPHENYLPHOSPHORANYLIDENESUCCINATE

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Photosensitized oxygenation of extremely stable P-ylides, dimethyl fluorenylidenetributyl- and triphenylphosphoranylidenesuccinate, afforded dimethyl fluorenylideneoxalacetate in good yield, when 9-fluorenone was employed as a photosensitizer.

Keywords: Allylidenephosphorane; photooxygenation; photosensitizer; oxalacetic acid

INTRODUCTION

In our continuing effort to exploit new reactions of stable P-ylides, we are surveying the key reactions to enhance the reactivity of the ylides. A strategy is based on internal redox property and an electron-transfer nature of them.[1] Another is considered to be a singlet oxygenation in self-sensitized manner of the ylide,[2] reported previously by us. Many stable ylides have aryl groups attached to a carbanion center, and the group contributes to the stabilization of ylides. This group is expected also to play a role as a photosensitizer for efficient photoreaction of the P-ylide. The reaction is potentially useful as a synthetic procedure for the preparation of unique

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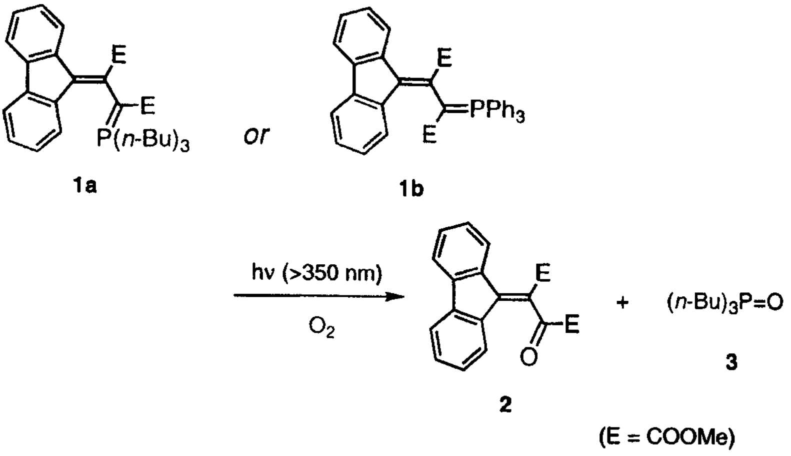
carbonyl compounds. In order to further examine the applicability of this method, we wish to report herein on the singlet oxygenation of extremely stable P-ylide, allylidenephosphorane derivatives. Those P-ylides have been described in literature,[3] though the detailed structure, physical properties and chemical reactivities have not yet been fully elucidated. As is shown in our recent paper,[1] the ylide is very stable and does not react with usual ketonic compounds. It reacts only with carboxylic acids to give acid anhydrides.

RESULTS AND DISCUSSION

Extremely stable allylidene P-ylides having a tri-*n*-butyl (**1a**) and a triphenyl (**1b**) groups on phosphorus[4] are a red and an orange crystals respectively, thus self-sensitized photooxygenation reactions may be expected due to their good chromophoric group (fluorenylidenemethyl carbanion). Both compounds **1a** and **1b** exhibit a strong absorption at *ca.* 450 nm (in MeCN; $\epsilon \sim 10{,}000$) in UV-VIS spectra. Hoping for the enhanced photooxygenation reactivity of them, several photochemical and thermal reactions were examined as shown in TABLE I.

The results are as follows. None of an oxidized product was observed in thermal reaction of **1a**(entry 1) in toluene for 24 h under O_2 circumstance. The stability of **1** is thus clearly demonstrated. Similarly, **1a** is stable upon direct photoirradiation (500W Xe lamp, >350 nm) in acetonitrile as is shown in an experiment of entry 2. By contrast, upon photoirradiation under the same conditions in the presence of oxygen, **1a** was oxidized to give products, dimethyl fluorenylideneoxalacetate (**2**)[5] in only 6% yield and tri-*n*-butylphosphine oxide (**3**) with large portion of recovery of **1a.**

Regarding the wavelength effect of irradiation, when the reaction mixture was irradiated with >420 nm-light, no oxygenation of **1a** was observed. The oxygenation reaction only occurred upon irradiation with >350 nm-light. It suggests that light with appropriate wavelength should be selected to induce efficient photooxygenation of the P-ylide. The region is analyzed by semiempirical molecular orbital calculations (MOPAC,[6] PM3 SCF-MO[7] and ZINDO[8]calculations) and absorption of a fluorenylidene moiety in **1** is located at *ca.*350-nm area of the UV-VIS spectra. Based on the results, we further examined a photosensitized oxygenation [sensitizer, 9-fluorenone (**4**); $E_T = 50.4$ kcal/mol[9]] to exploit more efficient oxidation procedure of **1a**. In this case (entry 4), the reaction pro-



ceeded completely to afford **2** quantitatively. The concentration of **4** was so adjusted (*ca.* 10 times higher than that of **1a**) that effectively absorbs the incident light at wavelength region of >350 nm. The same photooxygenation reaction of **1b**(entry 5) proceeded with lower efficiency than that of **1a**.[10] In order to elucidate the responsible species of oxygenation, effect of known singlet oxygen scavenger, DABCO (diazabicyclooctane),[11] was studied (entry 6) and it suppressed the reaction. Singlet oxygen is the most crucial candidate to induce this reaction as further evidenced by formation of **2** in the thermal reaction with diphenylanthracene endoperoxide (DPAP) (entry 7), a known thermal singlet oxygen generating agent.[12] As a result, it is found that the self-photosensitized singlet oxygenation of stable P-ylides, allylidenephosphoranes **1** occurred with low efficiency upon photoirradiation of **1** itself. The reactivity, however, was greatly improved by incorporating an external photosensitizer like **4**. The reason for lower efficiency of self-photosensitization of **1** is uncertain. Although the photophysical data of 9-fluorenylide ion composing **1** is not available, those of fluorene in reference has been reported.[13] All these values of fluorene suggest that photosensitizing ability of **1** seems to be inferior to those of **4**. In summary, the extremely stable allylidene P-ylides **1a** and **1b** have been successfully oxidized in photosensitized manner (sensitizer; 4), in contrast to self-sensitized photooxygenation of fluorenylidene P-ylides reported previously.[2] It seems applicable to the convenient preparation of oxalacetic acid derivatives.

TABLE I Photochemical and Thermal Oxygenation Reactions of Allylidenephosphoranes (**1a** and **1b**)

Entry	*Ylide* *(Conc. × 10^3 M)*	*Reaction Conditions*^{a}					*Yield (%)*^{b}	
		hv (>350 nm) or Δ	*Temp. (°C)*	*Time (h)*	*Atmosphere*	*Additive (Conc. × 10^3 M)*	***1***	***2***
1	**1a** (9.84)	Δ	110	24	O_2	-	100	0
2	**1a** (4.08)	hv	RT	8	Ar	-	100	0
3	**1a** (4.05)	hv	RT	8	O_2	-	94	6
4	**1a** (4.17)	hv	RT	8	O_2	**4**^{c} (55)	0	100
5	**1b** (3.62)	hv	RT	8	O_2	**4**^{c} (56)	56	44
6	**1a** (4.09)	hv	RT	8	O_2	**4**^{c} (55) DABCO^d (9.27)	>90	trace
7	**1a** (19.5)	Δ	80	15	Ar	DPAP^e (39.4)	-	27

[a] Thermal reactions in dry toluene (entry 1) and in dry benzene (entry 7). Other photochemical reactions were done in dry acetonitrile. [b] Yields were determined by ^{1}H NMR (400 MHz) spectrometry. [c] 9-Fluorenone. [d] Diazabicyclooctane. [e] 9,10-Diphenylanthracene endoperoxide.

EXPERIMENTAL

Upon irradiation of an acetonitrile solution (50 ml) containing dimethyl fluorenylidenetri-*n*-butylphosphoranylidenesuccinate (**1a**, 50 mg, 0.1 mmol) and 9-fluorenone (**4**, 250 mg, 1.4 mmol) under oxygen with a high-pressure mercury lamp (500 W, >350 nm) for 8 h, a yellow reaction mixture was obtained by evaporating the solvent. Excess **4** was removed by recrystallization from *n*-hexane and the residue was chromatographed on silica-gel (Merck, 230–400 mesh) eluted with 15% (v/v) EtOAc in *n*-hexane to give **2** (29 mg, 92%) as light yellow oil. Compound **3** (19 mg, 89%)was finally eluted with EtOAc as colorless crystals.

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[4] Single-crystal X-ray crystallographic studies revealed that the structure of **1a** is s-*cis* and that of **1b** is s-*trans* by our laboratory and the data correspond well with the energy optimized structures estimated by molecular orbital calculations (MOPAC PM3-SCF[7]).

[5] Physical data of compound **2**: MS (70 eV) m/z (%) : 322 (M^+, 16), 263 ($M-CO_2Me$, 100), 195 (MeO-Fluorene, 98), 176 ($M-COCO_2Me$, 28); HRMS (EI): Calcd. 322.0841, found 322.0860; ^1H NMR (400 MHz, $CDCl_3$) δ_{ppm} : 3.90 (3H, s), 3.91 (3H, s), 7.11 (1H, t, J=7.8 Hz), 7.22 (1H, t, J=7.8 Hz), 7.34 (1H, d, J=7.8 Hz), 7.32–7.43 (2H, m), 7.56 (2H, d, J=7.8 Hz), 8.06 (1H, d, J=7.8 Hz); ^{13}C NMR (100.4 MHz, $CDCl_3$) δ_{ppm}: 52.9, 53.6, 119.8, 120.1, 126.0, 126.2, 127.7, 127.8, 128.1, 131.9, 132.0, 135.5, 135.8, 142.2, 142.3, 149.8, 160.6, 164.8, 185.2; IR (Nujol) $\nu_{cm^{-1}}$: 2980m, 1730(broad)s, 1600m, 1460s, 1445m.

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