

THE REACTION OF PHOSPHORUS YLIDS WITH SINGLET OXYGEN

*Charles W. Jefford and Giacomino Barchietto,*

*Department of Organic Chemistry, University of Geneva,*

*1211 Geneva 4, Switzerland*

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Phosphorus ylids find great utility in synthesis where the best known reactions such as the Wittig and variants thereof are used for the construction of carbon-carbon bonds.<sup>1</sup> We now report a new, simple reaction of methoxycarbonylalkylidenephosphoranes with singlet oxygen to give  $\alpha$ -keto carboxylic esters.<sup>2</sup> The general procedure consists in placing the ylid in a solvent, such as chloroform, benzene or methanol, adding as sensitizer *meso*-tetraphenylporphin or rose bengal and then irradiating with light from a 500 W tungsten filament lamp while oxygen is passed through the solution.<sup>3</sup> After a few minutes, the solution is filtered from triphenylphosphine oxide and the  $\alpha$ -keto carboxylic ester is recovered in yields of 94-100%.

We present three typical and one atypical examples. The most clean-cut reaction is with methoxycarbonylbenzylidenetriphenylphosphorane (1) (Table 1).<sup>4</sup> Photo-oxygenation is rapid, 1 has a half-life of only a few minutes at 10<sup>0</sup>, and a quantitative yield of methyl phenylglyoxylate 2 is obtained. In methanol, the rate of reaction is twice as slow as that in chloroform and traces (1.4%) of uncharacterized substances are also formed. The behaviour of the isobutylidene-phosphorane (3) is strictly analogous (Table 1). High yields of methyl  $\alpha$ -keto-isobutyrate (4) are obtained (95-98%) in the haloforms and benzene, but an insignificantly lower yield (89%) accompanied by unspecified side products is found in methanol. Similarly, the ethylidene-phosphorane 5 reacts rapidly giving essentially methyl pyruvate 6 (94-98% yields) adulterated by small amounts of methyl acrylate epoxide (7) and tiny amounts of impurities (Table 1).

In all cases, singlet oxygen appears to be the reagent responsible inasmuch as replacing oxygen by nitrogen or adding diazobicyclo[2.2.2]octane (DABCO) ( $2.5 \times 10^{-4}$  M)<sup>5</sup> stops and retards

Table 1. Photo-oxygenation of Some Phosphoranes

$\text{P}=\text{C}(\text{R})\text{COOMe}$		$\xrightarrow{{}^1\text{O}_2}$	$\text{RCOCO}_2\text{Me} + \text{Side products}^e$	
Reactant <sup>a</sup>	Half-life <sup>b</sup>	Conditions <sup>c</sup>	Yield in % <sup>d</sup>	
<u>1</u> R=∅			<u>2</u>	
	4'20"	$\text{CDCl}_3/\text{TPP}$	100	-
	4'30"	$\text{CHCl}_3/\text{TPP}$	100	-
	6'15"	$\text{C}_6\text{H}_6/\text{TPP}$	100	-
	8'43"	$\text{CH}_3\text{OH}/\text{RB}$	98.6	1.4
<u>3</u> R=iPr			<u>4</u>	
	3'08"	$\text{CDCl}_3/\text{TPP}$	95	5
	3'30"	$\text{CHCl}_3/\text{TPP}$	94	6
	5'46"	$\text{C}_6\text{H}_6/\text{TPP}$	98	2
	7'18"	$\text{CH}_3\text{OH}/\text{RB}$	89	11
<u>5</u> R=Me			<u>6</u>	
	2'24"	$\text{CDCl}_3/\text{TPP}$	94	6 <sup>f</sup>
	2'36"	$\text{CHCl}_3/\text{TPP}$	95.4	4.6 <sup>g</sup>
	5'05"	$\text{C}_6\text{H}_6/\text{TPP}$	98.6	1.4
	6'37"	$\text{CH}_3\text{OH}/\text{RB}$	98	2.0 <sup>f</sup>

<sup>a</sup> Concentration of phosphorane was 0.2 M in 2.5 ml of solvent.

<sup>b</sup> Half-lives of reactant were estimated from the rate of absorption of oxygen assuming an equimolar reaction with substrate.

<sup>c</sup> The concentration of sensitizer, *meso*-tetraphenylporphyrin (TPP) or rose bengal (RB) was  $10^{-3}$  M. The temperature of the solution was  $12^\circ$  for 3, and  $10^\circ$  for 1 and 5.

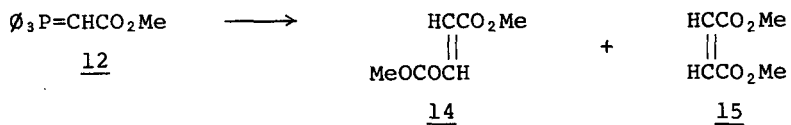
<sup>d</sup> Absolute yields were obtained by glc (5% OV-225 on Chromosorb WAW at  $190^\circ$ , carrier gas nitrogen). Internal standards were hexadecane (Fluka) for 1, pentadecane (Fluka) for 3, tridecane (Fluka) for 5.

<sup>e</sup> Except where specified, these were unidentified.

<sup>f</sup> The only side product was the epoxide of methyl acrylate (7).

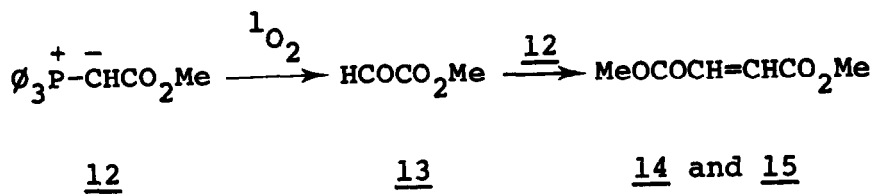
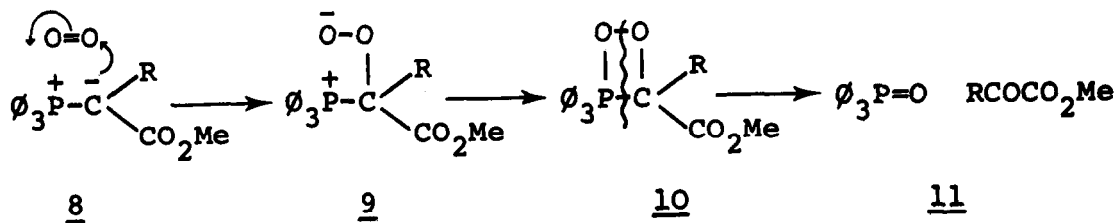
<sup>g</sup> 1.2% of 7 was also present.

Table 2. Photo-oxygenation of Methoxycarbonylmethylidene-triphenylphosphorane<sup>a</sup>



Half-life	Conditions	Yield in %
1'24"	CDCl <sub>3</sub> /TPP	89.9
1'32"	CHCl <sub>3</sub> /TPP	89.3
2'47"	C <sub>6</sub> H <sub>6</sub> /TPP	98.9
3'18"	CH <sub>3</sub> OH/RB	67.8

<sup>a</sup>The general remarks mentioned in Table 1 are valid



respectively the reaction. Auto-oxidation is also negligible since the adjunction of di-*t*-butylcresol ( $2.27 \times 10^{-4}$  M) to the reaction mixture scarcely affects the course or the rate of photo-oxygenation.<sup>6</sup>

We can safely assume that the mechanism is electrophilic attack<sup>7</sup> by a singlet oxygen molecule on the carbanionic centre (8) to create the zwitterionic peroxide 9.<sup>8</sup> Closure then occurs to the phosphetane 10 followed by cleavage to the product 11. Once the  $\alpha$ -keto ester forms it reacts no further with singlet oxygen, although as we have reported elsewhere,<sup>9</sup> the free acids themselves undergo oxidative decarboxylation. In principle, further reaction between the ylid and the newly formed  $\alpha$ -keto ester could occur, however in the three examples quoted, there was no evidence for this under the experimental conditions.<sup>10</sup> Nevertheless, in the case of the parent ylid, the methoxycarbonylmethylidenephosphorane (12), photo-oxygenation occurs readily, but immediately gives instead a mixture of dimethyl fumarate (14) and maleate (15) (Table 2). Evidently, the glyoxylic ester 13 as soon as it forms reacts rapidly with the ylid to give the observed products.

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#### REFERENCES AND NOTES

- (1) Reviews: H.J. Bestmann, *Angew. Chem. Internat. Edit* **4**, 645 (1965); *Bull. Soc. Chim. France* 1619 (1971); M. Schlosser, A. Piskala, C. Tarchini & Huynh Ba Tuong, *Chimia* **29**, 341 (1975).
- (2) For preparative methods see: L.R. Waters, *Chem. Rev.* **41**, 586 (1947); F. Weygand, W. Steglich & H. Tanner, *Liebigs Ann.* **658**, 128 (1962); G. Billek, *Org. Synth.* **43**, 49 (1963); M.G. Johnson, J.P. Turnbull & H.A. Crisp, *Ger. Offen.* **2**, 528, 786, *Chem. Abs.* **84**, 150492k (1976).
- (3) Our procedure (C.W. Jefford & A.F. Boschung, *Helv. Chim. Acta* **57**, 2242 (1974)) makes use of a Sylvania FFX 500 W lamp, cooled with air and surrounded by a pyrex glass water-cooled jacket. Light below 400 nm was stopped by an interposed Schott-Jena KV 418 filter.
- (4) The phosphoranes were prepared by standard methods: compounds 1 and 3 according to H.J. Bestmann & H. Schultz, *Liebigs Ann.* **674**, 11 (1964); compounds 5 and 12 following O. Isler, H. Gutmann, M. Montavon, R. Rüegg, G. Ryser & P. Zeller, *Helv. Chim. Acta* **40**, 1242 (1957).
- (5) DABCO quenches singlet oxygen (C. Ouannès & T. Wilson, *J. Am. Chem. Soc.* **90**, 6527 (1968).
- (6) K.U. Ingold, *Chem. Rev.* **61**, 563 (1961).
- (7) R.H. Young, *Chem. Comm.* 704 (1970); H.H. Wasserman & J.E. Van Werth, *J. Am. Chem. Soc.* **96**, 585 (1974); D.P. Higley & R.W. Murray, *ibid.* **96**, 3330 (1974).
- (8) I. Saito, M. Imuta, Y. Takahashi, S. Matsugo & T. Matsuura, *J. Am. Chem. Soc.* **99**, 2005 (1977); C.W. Jefford & C.G. Rimbault, *Tetrahedron Letters*, 2375 (1977).
- (9) C.W. Jefford, A.F. Boschung, T.A.B.M. Bolsman, R. Moriarty & B. Melnick, *J. Am. Chem. Soc.* **98**, 1017 (1976).
- (10) If photo-oxygenation was stopped at 50% absorption and then the solution was heated under reflux, the three expected products of Wittig reaction were obtained.