Ene Reactions of a Phosphaalkene as Enophile

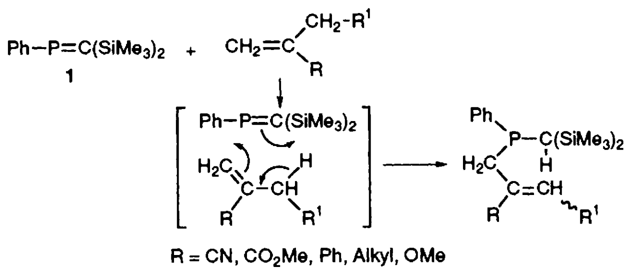
Masato Suzuki,*† Katsuhiko Sho, Katsuhide Otani, Tetsuya Haruyama and Takeo Saegusa

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606-01, Japan

The phosphaalkene phenyl[bis(trimethylsilyl)methylene]phosphine reacts readily with α,α-disubstituted alkenes containing allylic hydrogens to yield the ene reaction products.

The first success in isolating a stable phosphaalkene in 1976 triggered the explosive progress of the chemistry of low-coordinated trivalent phosphorus compounds including diphosphenes, phosphaalkynes, iminophosphines and phosphacumulenes.[1] Herein, we report a novel ene reaction of phosphaalkene as enophile which we discovered during investigations of the polymerization of phosphaalkenes. This finding extends the scope of pericyclic reactions of phosphaalkenes.[2]

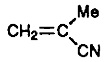
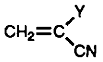
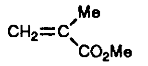
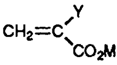
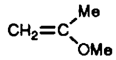
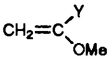
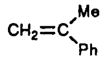
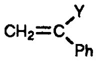
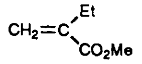
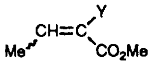
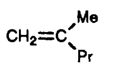
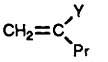
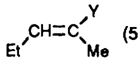
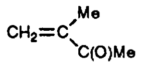
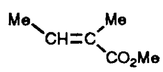
Phenyl[bis(trimethylsilyl)methylene]phosphine **1**[3] was reacted with several allylic alkenes (Scheme 1, Table 1) and the results were studied using ^{31}P NMR spectroscopy. For entries 1-5, a peak at δ 372 (for **1**) was quantitatively displaced by a peak assignable to a three-coordinated phosphine on the basis of its chemical shift value (δ −14 ~ −17). For entry 6, however, several ^{31}P NMR peaks were observed and the integral proportion of two main peaks due to three-coordinated phosphines was 70%. Since the phosphines produced tended to be oxidized by air, they were treated with H_2O_2 and the phosphine oxides formed‡ were isolated and characterized. ^1H, ^{13}C NMR and IR spectroscopies allowed us to conclude that the phosphines were ene reaction products.



R = CN, CO$_2$Me, Ph, Alkyl, OMe
R^1 = H, Alkyl

Scheme 1

Table 1 The ene reaction of phenyl[bis(trimethylsilyl)methylene]phosphine **1** with alkenes[a]

Entry	Alkene	T/°C (t/h)	Product[b]	δ_P
1	 $CH_2{=}C(Me)CN$	50 (12)	 $CH_2{=}C(Y)CN$	-15.6
2	 $CH_2{=}C(Me)CO_2Me$	50 (12)	 $CH_2{=}C(Y)CO_2Me$	-14.3
3	 $CH_2{=}C(Me)OMe$	50 (12)	 $CH_2{=}C(Y)OMe$	-14.1
4	 $CH_2{=}C(Me)Ph$	50 (29)	 $CH_2{=}C(Y)Ph$	-16.9
5	 $CH_2{=}C(Et)CO_2Me$	50 (13) 80 (14) 100 (9)	 $MeCH{=}C(Y)CO_2Me$ (E:Z = 70:30)	-16.0
6	 $CH_2{=}C(Me)Pr$	50 (12) 80 (12) 100 (6)	 $CH_2{=}C(Y)Pr$ (50)[c]  $EtCH{=}C(Y)Me$ (50)[c,d]	-18.0, -19.2
7	 $CH_2{=}C(Me)C(O)Me$	room temp.	Complex reaction	
8	 $MeCH{=}C(Me)CO_2Me$	150 (20)	Complex reaction	

[a] An equimolar mixture (0.23–0.38 mmol) of **1** and alkene was heated in 0.3 ml of PhCl. [b] Y = $CH_2P(Ph)CH(SiMe_3)_2$. Yield (evaluated from the *in situ* ^{31}P NMR spectrum) ≈100% (entries 1–5), 70% (entry 6). [c] The proportion of the main products. [d] The Z-isomer was not detected.

Ease of hydrogen transfer from the methyl and methylene groups and the stereoselectivity of the reaction depended on the substrate. Methyl α-ethylacrylate reacted more slowly than methyl methacrylate and produced a mixture of E and Z stereoisomers of the tri-substituted alkene (see entries 2 and 5). On the other hand, in the reaction of entry 6, the product proportion 50:50 indicated that hydrogen atoms shift from methyl and methylene groups at the same rate, and the tri-substituted alkene produced was exclusively the E-isomer.

It is noteworthy that electron-poor and -rich alkenes show almost the same reactivities. This finding is ascribable to the presence of a lone pair of electrons on the P in **1** and polarisation of the P=C bond making the phosphorus atom electron deficient and the carbon atom electron rich (Scheme 2).[4] Thus, the phosphorus atom of **1** is amphiphilic in showing reactivity towards both electron-poor and -rich positions.

$$Ph\text{-}\ddot{P}{=}C(SiMe_3)_2 \longleftrightarrow Ph\text{-}\overset{+}{\ddot{P}}\text{-}\overset{-}{C}(SiMe_3)_2$$

Scheme 2

The reaction of 3-methylbut-3-en-2-one with **1** gave too many products to be analysed (entry 7). It seems that the carbonyl group of the enone participated in the reaction to complicate the result. Steric hindrance exerted a serious influence on the reaction. Methyl tiglate was inactive and forced heating at 150 °C induced a set of complicated reactions (entry 8). Another stable phosphaalkene, mesityl(diphenylmethylene)phosphine was inert under the same reaction conditions as that of **1**, while forced heating at 150 °C resulted in a complicated reaction.

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Footnotes

† *Present address*: Division of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 601-01, Japan

‡ One of two C–SiMe$_3$ bonds of the phosphine oxides was easily hydrolysed to a C–H bond by prolonged contact with aq. H_2O_2 or by exposure to moisture in the air at ambient temperature for several days. Another trimethylsilyl group was eliminated by treatment with a saturated solution of KF in MeOH.

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