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Detection and Reaction of Oxaphosphetanes Derived from Benzaldehyde and 1-Adamantylmethylidene Ylide

Hiroshi Yamataka,*[†] Tsutomu Takatsuka, and Terukiyo Hanafusa

The Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567, Japan and Institute for Fundamental Research of Organic Chemistry, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812-81, Japan

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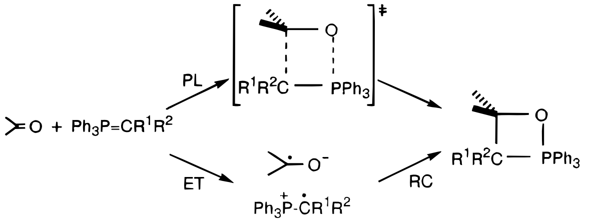
The Wittig reaction of (1-adamantylmethylidene)triphenylphosphorane ($Ph_3P{=}CH(1\text{-}Ad)$) with benzaldehyde was investigated, and the results were compared with those of other ylides. The substituent effect in the reaction of the ylide with benzaldehydes was determined by competition experiments, which gave a Hammett ρ value of 3.2. The ρ value is much larger than those reported for analogous reactions of $Ph_3P{=}CH(CH_2)_2CH_3$ ($\rho = 0.20$) and $Ph_3P{=}CH(CH_3)_2$ ($\rho = 0.59$), indicating that the reaction mechanism differs for $Ph_3P{=}CH(1\text{-}Ad)$ and the other ylides. The cis/trans ratio of the product alkene is 74/26 for the reaction with the parent benzaldehyde and highly depends on the position of the substituent; ortho substituted benzaldehydes gave the trans alkenes up to 90%. Monitoring the reaction by means of ^{31}P NMR revealed that both cis and trans oxaphosphetane intermediates were formed and that the formation and decomposition of the cis oxaphosphetane are 7−12 times faster than those of the trans oxaphosphetane. From the comparison of the reaction of $Ph_3P{=}CH(1\text{-}Ad)$ + benzaldehyde with those of $Ph_3P{=}CH(CH_2)_2CH_3$ + benzaldehyde and benzophenone, and $Ph_3P{=}CH(CH_3)_2$ + benzophenone, it was concluded that all the reactions with these nonstabilized ylides proceed via an electron-transfer mechanism and that the rate-determining step changes from the electron transfer step to that of radical combination when the substrate or ylide becomes more sterically demanding.

The Wittig reaction of benzaldehyde with a phosphorus ylide proceeds via one of two reaction pathways depending on the nature of the ylide (eq 1).[1,2] It has previously been shown that the reaction with a semistabilized ylide (benzylidenetriphenylphosphorane, **1**) proceeded via the direct polar addition (PL) mechanism[3] and gave a mixture of cis/trans alkenes,[4] whereas the reaction with a nonstabilized ylide ($Ph_3P{=}CH(CH_2)_2CH_3$, **2**) yielded preferentially the cis alkene[5,6] via an initial electron transfer (ET) from the ylide to benzaldehyde.[2] The mechanistic difference is due to a different ability of the ylides to transfer an electron to benzaldehyde. These conclusions were based on carbonyl carbon-14 kinetic isotope effects and substituent effects on the oxaphosphetane formation step as well as on the enone-isomerization and dehalogenation probe experiments.[2]

The reaction of nonstabilized ylides with benzaldehyde differ in many mechanistic respects from that with benzophenone.[1,2] Although both reactions proceed through oxaphosphetane intermediates, the kinetic stability of the intermediates is different under typical reaction conditions; the lifetime is long for that from benzaldehyde and short for that from benzophenone.[6a,7,8] Furthermore, the mechanism of the oxaphosphetane formation step is different for the two substrates; the ^{14}C isotope effects and the substituent effects showed that the reaction of benzaldehyde with nonstabilized ylides proceeds via rate-determining ET to give a radical ion pair that is followed by fast radical coupling (RC), whereas the oxaphosphetane from benzophenone is formed via fast ET and slow RC processes.



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In order to clarify the origin of the mechanistic difference between the two reactions, and also to understand more the mechanism of the Wittig reaction of nonstabilized ylides, we have carried out the reaction of benzaldehyde with 1-adamantylmethylidene ylide **3** (eq 2). The aforementioned mechanistic difference may arise from the large steric bulk of benzophenone which makes the access of the ylide carbon center to the carbonyl carbon difficult and thus the RC step becomes rate determining. If this rationalization is correct, then due to its steric bulkiness, the RC step for **3** is expected to be slowed down, which would make the RC step rate determining even in the reaction with benzaldehyde.

[†] Kyushu University.

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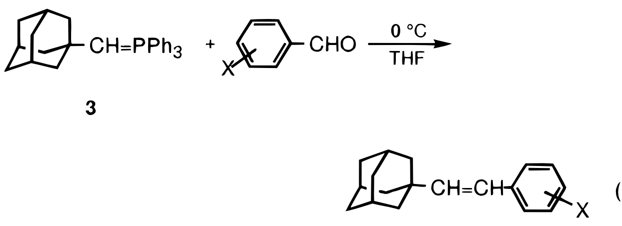

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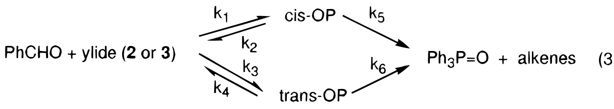
(2)

Results and Discussion

Benzaldehyde reacts with butylidenetriphenylphosphorane (**2**) or isopropylidenetriphenylphosphorane (**4**) quickly at −78 °C to form the corresponding oxaphosphetane, which then decomposes slowly at 0 °C to give alkene and triphenylphosphine oxide.[1] By contrast, it was found that the reaction of **3** with benzaldehyde is relatively slow at −50 °C and that the rates of the formation and the decomposition of the oxaphosphetane intermediate are similar. The ^{31}P NMR monitoring of the reaction under the Li-salt free conditions gave a stacked plot illustrated in Figure 1. In addition to the signals of **3** and $Ph_3P{=}O$, those of cis (−57.3 Hz relative to Ph_3P) and trans (−61.7 Hz) oxaphosphetanes were observed. The amount of cis oxaphosphetane increases quickly at the early stage of the reaction and then decreases, while the amount of trans oxaphosphetane increases gradually. By assuming a simple reaction scheme (eq 3, ylide = **3**), it was possible to compute rate constants of the six processes by matching the observed and the calculated time dependence of the four species. Maryanoff and the co-workers have carried out a similar treatment for the reaction of benzaldehyde with **2** under both Li-salt free and Li-salt present conditions.[6a] They found that although little or no "drift" of the stereochemistry of the oxaphosphetane was detected for the Li-salt free reaction, the reaction in the presence of LiBr brought about considerable "stereochemical drift". By following the concentration changes of a pair of oxaphosphetanes and the product, the four rate constants were obtained; in this reaction, the formation of the oxaphosphetane is too fast to follow and only the rate constant ratio, k_1/k_3, could be estimated.[6a] The reaction of benzophenone with **4** has also been followed previously in a similar manner but there is no cis/trans discrimination in this reaction.[8] The rate constants for the three sets of reactions are summarized in Table 1.[9]



(3)

Several important points are apparent in Table 1. (1) The oxaphosphetane formation rate constants are of the order of 10^{-3}–10^{-4} L mol^{-1} s^{-1} for **3**. These rates are much slower than those for **2**; the oxaphosphetane formation is too fast to follow even at −78 °C for **2**. The results indicate that the C−C bond formation step suffers a large steric effect for **3** as expected. In contrast to this, both oxaphosphetane reversal and decomposition appear to occur in similar rates for **3** and **2** if the effect of temperature is taken into consideration, suggesting that the steric requirements at the reversal and decomposition transition states are similar to that at the intermediate. (2) The cis oxaphosphetane forms 11.8 times faster than the trans oxaphosphetane, in accord with a general trend of high cis selectivity in the reaction of nonstabilized ylides with benzaldehyde. (3) The cis oxaphosphetane decomposes to give products 11.7 times faster and reverts to the reactants 6.8 times faster than the trans counterpart; thus the cis oxaphosphetane is kinetically less stable than the trans oxaphosphetane. The faster formation and the faster backward reaction of the cis oxaphosphetane compared with the trans oxaphosphetane are the origin of the "stereochemical drift" observed in the reaction of nonstabilized ylides with benzaldehyde.[6a] (4) Equilibrium constants between the reactants (benzaldehyde + **3**) and the oxaphosphetanes are 118 L mol^{-1} and 68 L mol^{-1} for the cis and the trans oxaphosphetane. These numbers are in between those for benzaldehyde + **2** (too large to determine) and benzophenone + **4** (3.3). (5) Fractionation at the oxaphosphetane (k_5/k_2) is 2.2 for cis and 1.3 (k_6/k_4) for trans. The values are similar for the reaction of benzophenone + **4** (1.8).

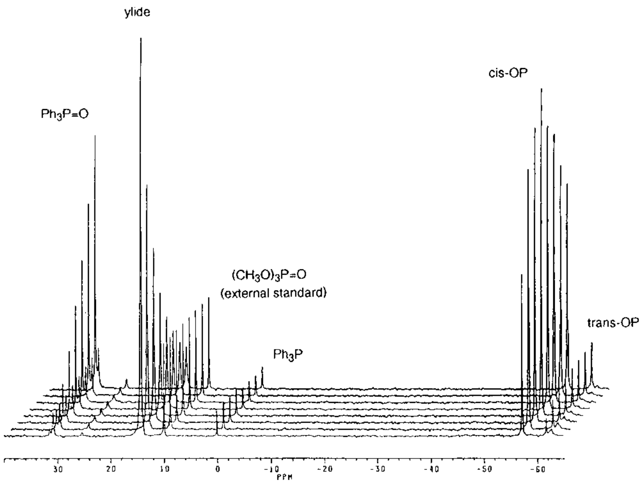


Figure 1. ^{31}P NMR stacked plot for the reaction of benzaldehyde with **3** at −50 °C. The aldehyde and ylide concentrations are 0.15 mol L^{-1} each.

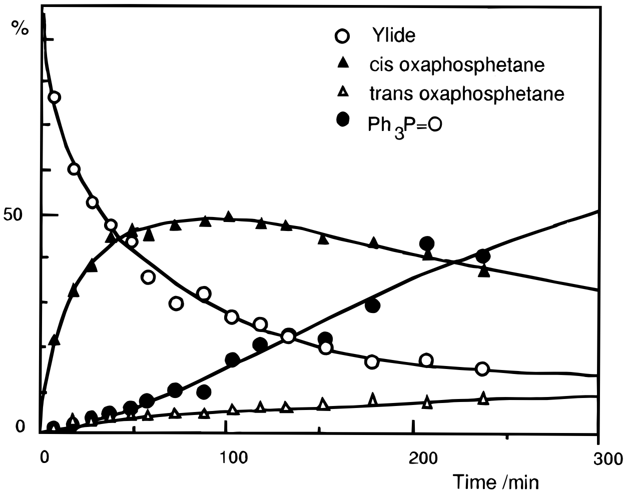


Figure 2. Variations of amounts of **3**, cis and trans oxaphosphetanes, and $Ph_3P{=}O$ with time in the reaction of benzaldehyde with **3** at −50 °C in THF.

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(9) Reliability of these rate constants were estimated by carrying out a series of simulation procedures with slightly different rate constants. The use of k_1 that is 10% larger than the value listed in Table 1 gave reasonable matching between the calculated and experimental results, but the use of the rate constant 20% larger than that in Table 1 resulted in unacceptable matching. Thus, the error limit of k_1 in the present derivation is 20%. Similarly, the error limit of k_3 is 20% and that of k_2 and k_5 is 40%. Since k_4 and k_6 are very small, values close to zero did not change the calculated curves very much, but they cannot be 5 times larger than those listed in Table 1.

Table 1. Estimated Rate Constants of Some Elementary Steps of the Wittig Reactions of Benzaldehyde with 2 and 3, and of Benzophenone with 4 in THF

step		rate constant	**3** + PhCHO[a] −50 °C	**2** + PhCHO[b] −30 °C	**4** + Ph$_2$C=O[c] 0 °C
oxaphosphetane	cis	k_1/L mol^{-1}s^{-1}	3.3 × 10^{-3}	*d*	1.3 × 10^{-3}
formation	trans	k_3/L mol^{-1}s^{-1}	2.8 × 10^{-4}	*d*	
		k_1/k_3	11.8	3.50	
oxaphosphetane	cis	k_2/s^{-1}	2.8 × 10^{-5}	1.39 × 10^{-4}	4.0 × 10^{-4}
reversal	trans	k_4/s^{-1}	4.1 × 10^{-6}	0.9 × 10^{-5}	
		k_2/k_4	6.8	15.4	
oxaphosphetane	cis	k_5/s^{-1}	6.2 × 10^{-5}	4.78 × 10^{-5}	7.0 × 10^{-4}
decomposition	trans	k_6/s^{-1}	5.3 × 10^{-6}	7.90 × 10^{-5}	
		k_5/k_6	11.7	0.61	

[a] Under Li-salt free conditions. [b] Under Li-salt present conditions. Data taken from reference 3a. [c] Data taken from reference 8. [d] Too fast to follow.

Table 2. Cis/Trans Product Ratio in the Wittig Reaction of Substituted Benzaldehydes with 3 and 1 in THF at 0 °C

	%cis	
substituent	**3**[a]	**1**[b]
p-OMe	*c*	38.7
m-OMe	*c*	46.3
o-OMe	*c*	83.7
p-Me	69.3	38.6
m-Me	67.2	38.0
o-Me	29.0	37.4
H	74.0	42.9
p-Cl	70.0	43.6
m-Cl	71.7	43.9
o-Cl	11.3	86.3
p-F	67.9	*c*
o-F	17.7	*c*
m-CF$_3$	70.3	44.6
p-CF$_3$	71.0	*c*

[a] Average of two runs. Reproducibility is better than 0.5%. [b] Data taken from reference 3. [c] Not determined.

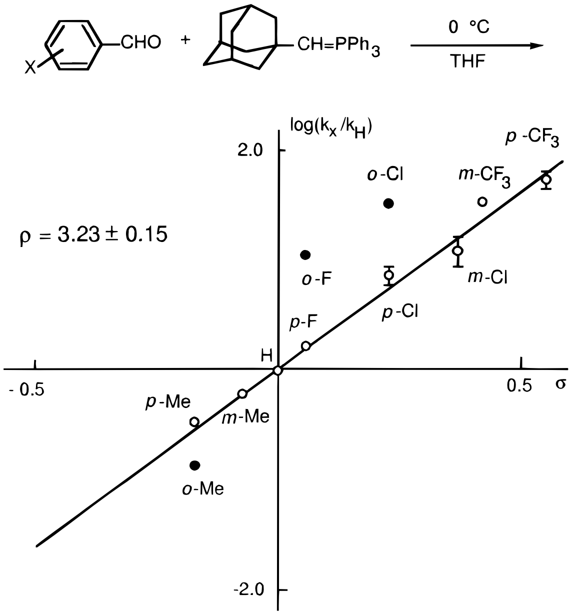

Figure 3. Variations of reactivity with the σ values for the reactions of substituted benzaldehydes with **3** at 0 °C in THF.

The cis/trans ratios of product alkenes were determined by GLC and ^{1}H NMR for the reactions of substituted benzaldehydes and **3**, and are summarized in Table 2. The cis/trans ratios for reactions with benzylidenetriphenylphosphorane **1** were also listed for comparison purpose. It should be pointed out at first that a considerable amount of trans alkene was detected in the reactions of a nonstabilized ylide, **3**, under the Li-salt free conditions. This is in sharp contrast to those for the reaction of benzaldehyde and **2**; here predominantly (>96%) cis alkene was formed under the Li-salt free conditions, and "stereochemical drift" occurred only when Li salt was present.[6a] Clearly the observed stereochemical drift is due to isomerization at the oxaphosphetane stage or later since the initial rate ratio (k_1/k_3 = 11.8) requires cis oxaphosphetane about 92% for X = H. The oxaphosphetane derived from **3** appears kinetically much less stable compared to the oxaphosphetane derived from **2**.

Substituents at the *meta*- and *para*-positions of benzaldehyde have little effect on the %cis value. Comparison of the present results with those reported previously for reactions of substituted benzaldehydes with **1** revealed that the two sets of reactions are similar in the *meta*- and *para*-substituent effect in that substituent electronic property has little influence on the %cis value. It is also apparent, however, that the effect of ortho substituents is quite different for the two series. First of all, *o*-Cl and *o*-Me derivatives gave higher %cis value for **1** in contrast to lower %cis for **3**. Second, *o*-Me showed little influence on the %cis value for **1**; this is also in sharp contrast to the *o*-Me effect in the reaction of **3**. The reason for the different ortho substituent effects for the two systems is not apparent, but the present results clearly indicate that the nature of the transition states is different for the two reaction systems.

Substituent effects on the overall reactivity were measured by competition experiments as reported previously.[8] The relative reactivities obtained are illustrated in Figure 3. Here the log(k_X/k_H) values for the ortho substituted derivatives were plotted against the corresponding σ_p constants and are indicated by closed circles. The points of *o*-Cl and *o*-F derivatives deviate upward from the correlation line. Such *ortho* halogen acceleration has previously been observed in the reaction of benzaldehyde with organometallic reagents and may be ascribed to a chelating interaction between the halogen atom and a reagent in the rate-determining transition state.[3,10] The large Hammett ρ value (3.23) obtained for the reaction of benzaldehydes and **3** clearly differs from the small ρ values observed previously for the reaction of benzaldehydes with **2** (0.20) and **4** (0.59) under the same reaction conditions, indicating that the nature of the rate-determining transition state is different from that for **2** or **4**.[2] The large ρ value for **3** is consistent with the polar mechanism as well as the ET-RC reaction pathway with the RC step rate determining. In the latter mechanism, the overall rate consists of the ET pre-

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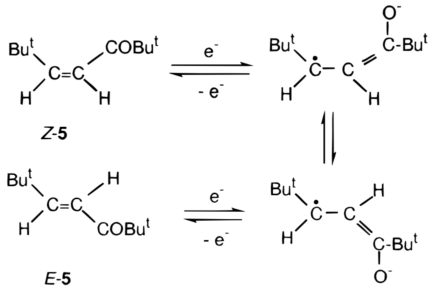
Table 3. *E*-*Z* Isomerization during the Reaction of *Z*-Enone with Various Ylides in THF at 0 °C[a]

ylide	time, min	recovered enone, *Z*:*E*
$Ph_3P{=}CHCH_3$	15	81.1:18.9
	30	70.4:29.6
$Ph_3P{=}CHPr$ (**2**)	15	76.6:23.4
	30	62.7:37.3
$Ph_3P{=}CHAd$ (**3**)	15	86.2:13.8
	30	68.8:31.2
$Ph_3P{=}CMe_2$ (**4**)[b]	15	86.1:13.9
	60	33.2:66.8
$Ph_3P{=}CHPh$ (**1**)[b]	15	98.2:1.8
	60	96.7:3.3
blank	60	98.5:1.5

[a] Wittig products were not detected. *E*:*Z* ratio was normalized; 100% = *E* + *Z*. [b] Data taken from reference 2.

equilibrium and the radical coupling rate, and the ρ value on the overall rate constant should be large positive[2] since the ρ value on the ET equilibrium is large positive.[11]

One way to distinguish between the two mechanistic alternatives is to examine a possible existence of the radical ion pair intermediate. The enone-isomerization probe is one of such criteria, and its usefulness has been proved in the literature.[2,12] Here, isomerization of the starting *Z*-enone (*Z*-**5**) to the *E*-enone (*E*-**5**) upon mixing with a reagent is taken as an indication of the occurrence of ET from the reagent to the enone (eq 4). Since the reduction potential of the *Z*-enone is more negative (−2.28 V vs SCE) than those of benzaldehyde (−1.84 V) and benzophenone (−1.82 V),[13] a positive response of the enone-isomerization probe then indicates the possible occurrence of ET to the aromatic aldehyde and ketone.



(4)

Table 3 lists the results of enone-isomerization probe experiment of **3**, together with those of other ylides. As reported previously, there is a clear-cut distinction between nonstabilized and semistabilized ylides.[2] It is apparent that ylide **3** exhibited a positive response in the probe experiment as in the other typical nonstabilized ylides, whereas the semistabilized ylide showed a negative response. Therefore it is reasonable to assume that the reaction of benzaldehyde with **3** proceeds through the same reaction pathway with other nonstabilized ylides, *i.e.* the ET-RC route, to give the oxaphosphetane intermediate.

It should be noted that although the enone-isomerization probe indicates the possible involvement of an ET process in the reaction, it does not necessarily mean that the ET process is on the main reaction coordinate. However, the combined use of several criteria, which include, in addition to the enone-isomerization probe, substituent effects on the reactivity, the carbonyl-carbon kinetic isotope effect, and the dehalogenation probe experiment, strongly suggested that the ET process is indeed involved in the main reaction pathway of the reactions of benzaldehyde with nonstabilized ylides.[2]

The combination of the substituent effect on reactivity and the probe experiment revealed that the reaction of **3** with benzaldehyde proceeds via the ET-RC reaction route to oxaphosphetane with the RC step rate determining. Thus, there occurs changeover of the rate-determining step from the ET step for ylides **2** and **4** to the RC step for **3**, and this mechanistic difference can be rationalized in terms of different steric requirement at the RC transition state. For less sterically demanding ylides (**2** and **4**) the RC step is lower in energy than the ET step, whereas for sterically demanding ylides **3**, the RC transition state becomes less stable. The occurrence of the mechanistic changeover is thus fully consistent with the Wittig reaction mechanism in which the radical ion pair species is a meaningful intermediate. Finally, the observed different effects of ortho substituents on the product cis/trans ratio in the reactions of benzaldehyde with **3** and **1** can be considered to arise from different reaction pathways of the two reactions, RC-ET for **3** and PL for **1**.

Experimental Section

Materials. THF was dried over sodium/benzophenone and distilled immediately before use. All substituted benzaldehydes were commercially available and purified by either distillation or recrystallization. 1-(Adamantylmethyl)triphenylphosphonium bromide was obtained by heating a mixture of triphenylphosphine (5.7 g, 22 mmol) and 1-adamantylmethyl bromide (5.0 g, 22 mmol) at 200 °C for 23 h. The reaction mixture was dissolved in $CHCl_3$, and colorless precipitates were collected by adding benzene. Recrystallization from EtOH/Et_2O gave 1-(adamantylmethyl)triphenylphosphonium bromide as a complex with a molecule of EtOH: 9.94 g (84%), mp. 267−71 °C. ^{1}H NMR (360 MHz, $CDCl_3$) δ 8.18−7.65 (m, 15H), 3.82 (d, J = 12.1 Hz, 2H), 3.71 (q, J = 7.03 Hz, 2H), 1.81−1.51 (m, 15H), 1.23 (t, J = 7.03 Hz, 3H). Anal. Calcd for $C_{31}H_{38}BrOP$: C, 69.27; H, 7.07; Br, 14.96; P, 5.76. Found: C, 69.46, H, 7.18, Br, 14.88, P, 5.73. The phosphonium bromide was then dissolved in $CHCl_3$ again, and benzene was added to obtain a colorless precipitate. This salt was suggested by ^{1}H NMR to contain a molecule of benzene instead of EtOH and was used in preparation of ylide **3**. (*Z*)-2,2,6,6-Tetramethylhept-4-en-3-one was synthesized as described in the literature.[14]

Reactions. All reactions were carried out under dry nitrogen using the Schlenk tube technique.[15] Ylide solution was prepared by adding an equimolar amount of sodium hexamethyldisilazide (NaHMDS, 1.0 M Aldrich) to a suspension of (1-adamantylmethyl)triphenylphosphonium bromide in THF at 0 °C. The Wittig reactions were followed by GLC or ^{31}P NMR.

The ^{31}P NMR monitoring of the reaction of benzaldehyde with **1** was carried out as reported before.[8] In a flame-dried NMR test tube (10 mm ∅) were placed a capillary that contains $(MeO)_3P{=}O$ in $CDCl_3$ (215 mg/L, internal reference) and a 2.25 mL THF solution of **3** (0.2 M) that was prepared from equimolar amount of (1-adamantylmethyl)triphenylphosphonium bromide and NaHMDS. The solution was then solidified at liquid N_2 temperature. To this was added a THF solution of benzaldehyde (0.75 mL, 0.6 M), and the tube was sealed. The Wittig reaction was followed at −50 °C probe

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temperature. The spectra were recorded on a Bruker 360M operating at 146 MHz for phosphorus. The conditions of ^{31}P measurements were chosen to ensure that the relaxation times of the species (determined by the T_1 null method) were sufficiently short for accurate integrals. The estimated reproducibility of the intensity was less than 5%, and the results from the kinetic treatment should be taken semiquantitatively.[16]

The relative reactivities of substituted benzaldehydes with **1** were determined at 0.0 ± 0.1 °C in THF by competition experiments as described previously.[8] Each Wittig reaction gave the expected alkenes, and no other products were detected. All product alkenes were characterized by ^1H NMR. Except for the parent compound, the products were obtained as mixtures of cis and trans alkenes. The chemical shifts of substituted *cis*- and *trans*-1-phenyl-2-(1-adamantyl)ethene derivatives are as follows: cis; H, δ 7.29−7.16 (m, 5H), 6.39 (d, J = 12.8, 1H), 5.36 (d, J = 12.8 Hz, 1H), 1.86−1.25 (m, 15H). trans; H, δ = 7.37−7.14 (m, 5H), 6.24 (d, J = 16.1, 1H), 6.10 (d, J = 16.1 Hz, 1H), 2.03−1.68 (m, 15H). *o*-Me, 7.48−7.09 (m, 4H), 6.42 (d, J_{trans} = 16.1, 1H), 6.23 (d, J_{cis} = 12.6, 1H), 5.96 (d, J_{trans} = 16.1 Hz, 1H), 5.37 (d, J_{cis} = 12.6, 1H), 2.34 (s, 3H, cis), 2.33 (s, 3H, trans), 2.04−1.54 (m, 15H). *m*-Me, 7.24−6.97 (m, 4H), 6.35 (d, J_{cis} = 12.8, 1H), 6.21 (d, J_{trans} = 16.1, 1H), 6.08 (d, J_{trans} = 16.1 Hz, 1H), 5.33 (d, J_{cis} = 12.8, 1H), 2.33 (s, 3H), 2.02−1.57 (m, 15H). *p*-Me, 7.18−6.98 (m, 4H), 6.28 (d, J_{cis} = 12.6, 1H), 6.13 (d, J_{trans} = 16.1, 1H), 5.97 (d, J_{trans} = 16.1 Hz, 1H), 5.25 (d, J_{cis} = 12.6, 1H), 2.25 (s, 3H, cis), 2.23 (s, 3H, trans), 1.95−1.47 (m, 15H). *o*-Cl, 7.52−7.07 (m, 4H), 6.62 (d, J_{trans} = 16.1, 1H), 6.20 (d, J_{cis} = 12.6, 1H), 6.07 (d, J_{trans} = 16.1 Hz, 1H), 5.44 (d, J_{cis} = 12.6, 1H), 2.03−1.53 (m, 15H). *m*-Cl, 7.29−7.08 (m, 4H), 6.30 (d, J_{cis} = 13.0, 1H), 6.18 (d, J_{trans} = 16.1, 1H), 6.06 (d, J_{trans} = 16.1 Hz, 1H), 5.37 (d, J_{cis} = 12.6, 1H), 2.03−1.51 (m, 15H). *p*-Cl, 7.29−7.08 (m, 4H), 6.30 (d, J_{cis} = 13.0, 1H), 6.18 (d, J_{trans} = 16.1, 1H), 6.06 (d, J_{trans} = 16.1 Hz, 1H), 5.37 (d, J_{cis} = 13.0, 1H), 2.03−1.51 (m, 15H). *o*-F, 7.48−6.96 (m, 4H), 6.41 (d, J_{trans} = 16.5, 1H), 6.16 (d, J_{cis} = 12.6, 1H), 6.16 (d, J_{trans} = 16.5 Hz, 1H), 5.50 (d, J_{cis} = 12.6, 1H), 2.04−1.54 (m, 15H). *p*-F, 7.36−6.93 (m, 4H), 6.32 (d, J_{cis} = 12.8, 1H), 6.20 (d, J_{trans} = 16.3, 1H), 6.00 (d, J_{trans} = 16.3 Hz, 1H), 5.36 (d, J_{cis} = 12.8, 1H), 2.02−1.54 (m, 15H). *m*-CF_3, 7.60−7.25 (m, 4H), 6.36 (d, J_{cis} = 12.6, 1H), 6.27 (d, J_{trans} = 16.3, 1H), 6.16 (d, J_{trans} = 16.3 Hz, 1H), 5.44 (d, J_{cis} = 12.6, 1H), 2.05−1.52 (m, 15H). *p*-CF_3, 7.58−7.25 (m, 4H), 6.27 (d, J_{trans} = 16.3, 1H), 6.19 (d, J_{trans} = 16.3 Hz, 1H), 2.05−1.64 (m, 15H). The cis/trans product ratio was determined as reported before.[3] In a standard procedure, 1.0 mL of THF solution (0.1 M) of ylide was added at 0 °C to 1.0 mL of THF solution (0.1 M) of benzaldehyde, and the solution was allowed to react for 30 min. The reaction mixture was worked up in a usual manner and subject to GLC analysis (2-m glass column packed with 3% PEG-HT) to determine the product ratio. The fraction of reaction was more than 70% except for less reactive substrates such as Me-substituted benzaldehydes. We could not find serious dependence of the product ratio on the fraction of reaction, and thus the qualitative discussion given in text is viable. Enone-isomerization experiments were carried out as reported previously.[2]

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(16) For kinetic experiments by use of ^{31}P NMR, see: Sawada, M.; Takai, Y.: Chong, C.; Hanafusa, T.; Misumi, S. *Tetrahedron Lett.* **1985**, *26*, 5065.