

THE MECHANISM OF THE REACTION OF P-YLIDES WITH DICHLOROCARBENE

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Abstract—Relative rates of the reaction of ring-substituted α -carbomethoxybenzylidetriphenylphosphoranes with dichlorocarbene have been measured. The results and some information concerning the structural dependence of other P-ylides on yields strongly support a mechanism which involves a rate-determining attack of the carbene on a P-ylide followed by rapid elimination of a phosphine. In addition, the large differences in reactivity observed for fluorenylidene-, indenylidene- and cyclopentadienylidene-triphenylphosphorane could be explained from the relevant π -electron localization energies calculated by the simple LCAO-MO method.

IN PREVIOUS papers,¹ we described the formation of haloölefins by the reaction of P-ylides with halocarbenes. This reaction apparently involves the essence of the well-known Wittig reaction, and this suggests an analogous mechanism involving an electrophilic attack of a halocarbene on the α -carbon of a P-ylide. In order to confirm this, the effect of substituents attached to the α -carbon or phosphorus atom of the ylides on the reactivity towards a fixed halocarbene was examined.

As is seen in Table 1, an electron-releasing group, such as methyl, on the α -carbon increased the yield of the product, while an electron-attracting group such as carbomethoxy decreased it. An increase in yield also resulted when three phenyl groups attached to the phosphorus atom were replaced with n-butyl groups, which probably release electrons towards the α -carbon via the phosphorus atom.²

For the purpose of quantitative comparisons, the relative reactivities of the following ylides, Ia ~ d and II, towards dichlorocarbene generated *in situ* from sodium trichloroacetate were determined by the competition method. In view of comparatively low yields of the reaction, the estimation was carried out in the range of 20 ~ 30% total yield of two dichloroölefins. The proportions of two haloölefins formed were determined by GLC analyses. The results are given in Table 2. Though no significant differences among their reactivities were observed, the order of relative rates agreed with the expectation from the data in Table 1.

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^{1a} R. Oda, Y. Ito and M. Okano, *Tetrahedron Letters*, 7 (1964); ^b *Bull. Inst. Chem. Research, Kyoto Univ. Japan*, 42, 217 (1964).

² In view of the stereospecificity in the addition of mono- and dichlorocarbenes to olefins, it is highly probable that halocarbenes are generally in the singlet state at usual reaction conditions. It has not yet been found whether the dichlorocarbene intermediates generated from different sources behave the same as divalent structures or not. Nevertheless, we may know the order of reactivities of P-ylides, as far as we refer to the data obtained under the same reaction conditions including the carbene generator.

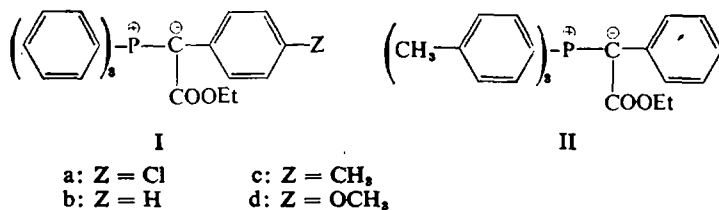


TABLE 1. STRUCTURAL DEPENDENCE OF P-YLIDES ON YIELDS*

P-ylide ^b	Carbene generator	Reaction conditions	Yield of haloölefin ^c
(Ph) ₃ P=C ₁₃ H ₉ ^d	PhCHCl ₂	70–75°, 12 hr in benzene	59%
(n-Bu) ₃ P=C ₁₃ H ₉ ^d	PhCHCl ₂	70–75°, 12 hr in benzene	77%
(Ph) ₃ P=CHCOOEt	CCl ₂ COONa	75–80°, 12 hr in dioxan	21%
(Ph) ₃ P=C(CH ₃)COOEt	CCl ₂ COONa	75–80°, 12 hr in dioxan	45%
(Ph) ₃ P=C(COOEt) ₂	CCl ₂ COONa	75–80°, 12 hr in dioxan	7%

* Data were taken from Ref. Ia and Ib.

* Each formula was represented as its ylene form.

* Based on ylide initially added.

* C₁₃H₉: fluorenylidene.

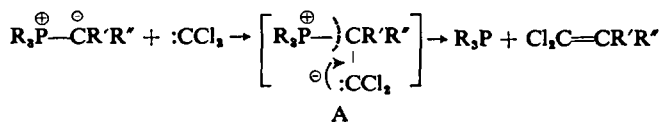
TABLE 2. RELATIVE RATES BY THE COMPETITION METHOD

Reaction conditions; in dioxan, 78 ± 1°, 3 ~ 4 hr

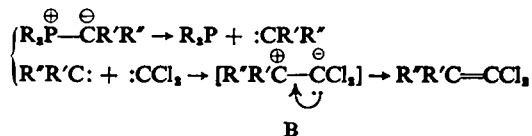
Starting P-ylides	Ratio of two olefins obtained	
	CCl ₂ =C(Ar)COOEt	CCl ₂ =C(C ₆ H ₅)COOEt
Ia + Ib	47	53
Ic + Ib	52	48
Id + Ib	55	45
Ia + II	44	56

Therefore, relative rates are given as follows: Ia:Ib:Ic:Id = 0.89:1.00:1.06:1.20 and II:Ib = 1.16:1.00

These results are consistent with the following mechanism, in which the rate-determining step consists of the attack of dichlorocarbene on the negatively-charged carbon atom of a P-ylide. If the elimination of a phosphine were rate-determining, an electron-releasing group on the phosphorus atom should retard it; however, in the reactions with tributyl- and tri-*p*-tolylphosphonium ylides, the reverse was observed as described above.



Another mechanism involving the intermediate formation of a carbene from a P-ylide followed by the combination with dichlorocarbene would be unacceptable, because no example of the utilization of stable P-ylides as a carbene generator are known.³



Previously we found that the reaction of carbethoxymethylene-triphenylphosphorane with chlorophenylcarbene gave only the *trans* isomer of ethyl β -chlorocinnamate and that under the experimental conditions the isomerization from the *cis* to the *trans* ester did not take place.^{1b} Such stereospecificity could be reasonably explained by assuming the former mechanism rather than the latter, because the life time of the intermediate B, as compared with that of A, is considered to be very short.

Considerable differences in reactivity of three P-ylides, fluorenylidene- (III), indenylidene- (IV) and cyclopentadienyldenetriphenylphosphoranes (V), would be attractive (Table 3). Although inertness of V in the Wittig reaction is known,⁴ no

TABLE 3. A COMPARISON BETWEEN REACTIVITY AND LOCALIZATION ENERGY FOR THREE STABLE P-YLIDES

P-ylide	III	IV ^b	V ^c
Reactivity towards dichlorocarbene ^a (yield of haloölefin)	44%	8% ^e	Unreacted
Localization energy ($-\beta$ unit)	1.83	2.00	2.21

^a Carbene generator: CHCl_2 , reaction conditions: 10–15°, 4 hr, in benzene. (Ref. 1b).

^b A new ylide (m.p. 213–214°). (Found: C, 86.32; H, 5.83. $\text{C}_{17}\text{H}_{11}\text{P}$ requires: C, 86.17; H, 5.59%.)

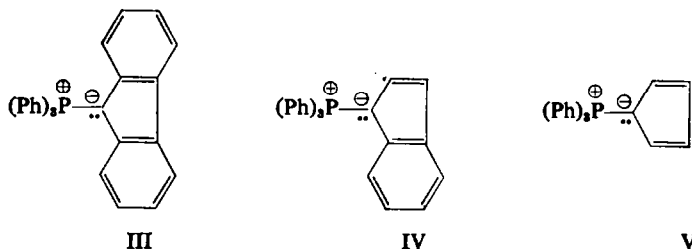
^c The product is a new compound (m.p. 57–58°). (Found: C, 61.32; H, 3.29; Cl, 35.61. $\text{C}_{10}\text{H}_4\text{Cl}_2$ requires; C, 60.91; H, 3.05; Cl, 36.04%.)

^e Inertness in the reaction with phenylchlorocarbene was also observed. (Ref. 1b).

reasonable explanation has ever been provided. Considering the reaction mechanisms, one may assume that the failure of our reaction and the Wittig reaction for V would be due to the relative difficulty in localization of one electron pair on its α -carbon atom. In order to visualize this situation, we have undertaken to calculate such localization energies for III ~ V, using the simple LCAO-MO method.

³ In the reaction of a benzoylphosphonium ylide with phenacyl bromide, the intermediate formation of benzoylcarbene from the ylide was provisionally suggested. However, it has been pointed out that such a possibility appears highly improbable in current view of P-ylide chemistry. See W. Kirmse, *Carbene Chemistry*, p. 117. Academic Press, New York, N.Y. (1964).

⁴ F. Ramirez and S. Levy, *J. Amer. Chem. Soc.* 79, 67 (1957).



In calculating the localization energies, we have employed the following approximate procedure. Since the ground state of P-ylides is likely to be a resonance hybrid of the ylide and ylene forms, the vacant $3d\pi$ orbital on the phosphorus atom must be taken into account. By replacing the common group $(\text{Ph})_2\text{P}$ with a single-orbital heteroatom X, we have simulated the three ylides with the corresponding fulvene homologs, in which the side-chain atom is regarded as less electronegative than carbon atom. The total π -electronic energies of the delocalized ground states were calculated by solving the secular equations required for the 14π -, 10π - and 6π -electron systems for III, IV and V, respectively. The total energies of the localized states are the same as those of the corresponding alternant hydrocarbons, i.e., biphenyl, styrene and butadiene. The localization energies are simply the differences between the above two energies.

The parameters used in the calculations are as follows:

$$\text{Coulomb integral of atom X } \alpha_x = \alpha + \delta_x\beta = \alpha - 0.5\beta.$$

$$\text{Exchange integral between atoms C and X } \beta_{cx} = \rho_{cx}\beta = 0.5\beta.$$

Here, the δ_x and ρ_{cx} values were determined from the electronegativity of P atom and the bond distance between P and C, respectively.⁵ The results obtained are included in Table 3. Such differences in localization energy would suffice to explain their different reactivities.

EXPERIMENTAL

Materials. The following ylides were prepared from the corresponding phosphines and bromides according to Isler *et al.*⁶ They are all new compounds.

α -Carbethoxybenzylidenetriphenylphosphorane. m.p. 137–138°. (Found: C, 79.34; H, 6.02. $\text{C}_{28}\text{H}_{26}\text{O}_2\text{P}$ requires: C, 79.23; H, 5.94%.)

*α -Carbethoxy(*p*-chloro)benzylidenetriphenylphosphorane.* m.p. 153.5–154.5°. (Found: C, 73.52; H, 5.34. $\text{C}_{28}\text{H}_{24}\text{ClO}_2\text{P}$ requires: C, 73.28; H, 5.27%.)

*α -Carbethoxy(*p*-methyl)benzylidenetriphenylphosphorane.* m.p. 127–130°. (Found: C, 79.71; H, 6.29. $\text{C}_{29}\text{H}_{28}\text{O}_2\text{P}$ requires: C, 79.43; H, 6.21%.)

*α -Carbethoxy(*p*-methoxy)benzylidenetriphenylphosphorane.* m.p. 161.5–162.5°. (Found: C, 76.24; H, 5.69. $\text{C}_{29}\text{H}_{28}\text{O}_3\text{P}$ requires: C, 76.64; H, 5.99%.)

*α -Carbethoxybenzylidenetri(*p*-tolyl)phosphorane.* m.p. 177–178°. (Found: C, 79.92; H, 6.60. $\text{C}_{31}\text{H}_{30}\text{O}_2\text{P}$ requires: C, 79.81; H, 6.70%.)

Competition experiments. A typical example is given below. In 150 ml dry dioxan 3.18 g (0.0075 mole) *α -carbethoxybenzylidenetriphenylphosphorane* and 3.44 g (0.0075 mole) *α -carbethoxy(*p*-chloro)benzylidenetriphenylphosphorane* were dissolved, and then 11.13 g (0.06 mole) sodium trichloroacetate was added. The mixture was stirred under a N_2 atmosphere at $78 \pm 1^\circ$ for 3.5 hr

⁵ The use of different δ_x and ρ_{cx} values varying from 0 to -1 and from 0 to 1, respectively, did not affect the qualitative aspect of our conclusion.

⁶ O. Isler, H. Gutmann, M. Montavon R. Ruegg, G. Ryser and P. Zeller, *Helv. Chim. Acta* **40**, 1248 (1957).

and cooled. After a mixed precipitate of NaCl and the unreacted acetate was filtered off, the filtrate was distilled *in vacuo* to remove the solvent. The benzene solution of the residue was washed with 5% HBr, successively with water and then concentrated *in vacuo*. Excess pet. ether was added to the concentrate to remove triphenylphosphine oxide (probably formed during the working-up) and the supernatant portion was collected by decantation. After the evaporation of the solvent, the residual liquid was distilled up to 200° (bath temp) at 3 mm. (1 g). The GLC analysis (a 2 m column of containing Apiezon Grease L-Celite 545 (3:7), carrier gas He, at 200°) indicated that it was composed of 53% ethyl β,β -dichloro- α -phenylacrylate (VI) and 47% ethyl β,β -dichloro- α -*p*-chlorophenylacrylate (VII), without containing another component. In 4 individual experiments including the above, about the same ratios (VI:VII = $53 \pm 1\%:47 \mp 1\%$) were recorded. The authentic materials used here as references were prepared by the reaction of the corresponding P-ylides with sodium trichloroacetate in dioxan. Their analytical data, together with those of other reference compounds, are shown below.

Ethyl β,β -dichloro- α -phenylacrylate. b.p. 112–114°/2 mm. (Found: C, 54.32; H, 4.28; Cl, 29.27. $C_{11}H_{10}O_2Cl_2$ requires: C, 53.90; H, 4.11; Cl, 28.93%.)

*Ethyl β,β -dichloro- α -*p*-chlorophenylacrylate.* b.p. 115–117°/2 mm. (Found: C, 47.41; H, 3.24; Cl, 38.55. $C_{11}H_9O_2Cl_3$ requires: C, 47.26; H, 3.25; Cl, 38.10%.)

*Ethyl β,β -dichloro- α -*p*-tolylacrylate.* b.p. 125–128°/8 mm. (Found: C, 56.07; H, 4.86; Cl, 28.03. $C_{11}H_{11}O_2Cl_2$ requires: C, 55.62; H, 4.67; Cl, 27.41%.)

*Ethyl β,β -dichloro- α -*p*-methoxyphenylacrylate.* b.p. 118–121°/2 mm. (Found: C, 52.60; H, 4.48. $C_{11}H_{11}O_3Cl_2$ requires: C, 52.36; H, 4.36%.)

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