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The Pyrolysis and Photolysis of Triphenylphosphine-carbethoxymethylene in Solution[1]

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Although there have been intensive investigations of the reaction of phosphine-ylids,[2] the pyrolysis of ylid in solution has received little attention, except for an unstable ylid, triphenylphosphine-*n*-butoxymethylene, which was studied by Wittig *et al.*[3]

We have studied the pyrolysis of a typical stable ylid, triphenylphosphine-carbethoxymethylene (I), in cyclohexene, and compared the results with those of the photolysis of I, which was reported previously.[4] In this paper, we wish to report the novel observation that, in pyrolysis, only P=C bond fission occurs, while P-phenyl bond fission occurs preferentially in photolysis.

Results and Discussion

The results of the photolysis and pyrolysis of I in cyclohexene are summarized in Table 1.

As may be seen from Table 1, I exhibited considerable thermal stability.

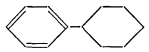
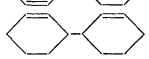
1) Organic Photochemical Reactions, Part XI. Part X; T. Kubota, K. Shima, S. Toki and H. Sakurai, *Chem. Commun.*, **1969**, 1462.

2) A. W. Johnson, "Ylid Chemistry," Academic Press, New York and London (1966), p. 88.

3) G. Wittig and W. Boll, *Chem. Ber.*, **95**, 2526 (1962).

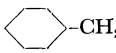
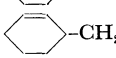
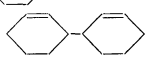
4) Y. Nagao, K. Shima and H. Sakurai, *Kogyo Kagaku Zasshi*, **72**, 236 (1969).

TABLE 1. PHOTOLYSIS[a] AND PYROLYSIS[b] OF $Ph_3P{=}CHCO_2C_2H_5$ (I) IN CYCLOHEXENE
(a) in quartz tube, I; 0.87mmol, cyclohexene; 40 m*l*, high pressure mercury lamp, 40 hr.
(b) I; 1.44 mmol, cyclohexene; 15 m*l*, *ca.* 180°C, 40 hr, conversion; 34%.

products	(a) mmol×10²	(a) Yield %	(a) Quantum yield, *Φ	(b) mmol×10²	(b) Yield %
	8.7	100	0.02	—	—
$CH_3CO_2C_2H_5$	0.7	8	—	—	—
 (III)	1.0	12	0.001	6.8	14
 (IV)	1.6	19	0.0007	2.5	5
	1.6	19	0.004	—	—
 (II)	4.1	—	0.01	8.8	—
$Ph_2P(O)OH$	1.5	16	—	—	—
Ph_3P	—	—	—	0.7	2

* Quantum yields were measured by use of a low pressure mercury lamp as a light source.

TABLE 2. PYROLYSIS OF $Ph_3P{=}CHCO_2C_2H_5$ (I) IN CYCLOHEXENE
I; 1.44 mmol, cyclohexene; 15 m*l*.
(a) di-*t*-butyl peroxide; 10 mg, after 24 hr, conversion; 31%.
(b) in the presence of air, at about 180°C, after 8 hr.

products	(a) mmol×10²	(a) Yield(%)	(b) mmol×10²	(b) Yield(%)
 (III)	3.5	8	28	20
 (IV)	0.9	2	1.2	0.9
 (II)	35	—	38	—
Ph_3P	0.7	1.7	0.2	0.1
Ph_3PO (V)	10.4	23.5	61	45

Before comparing the results of the photolysis with those of pyrolysis, it is necessary to check if the pyrolysis of I was induced by the attack of the radicals produced in this system. Therefore, a typical radical initiator, di-*t*-butyl peroxide, was added to the solution in order to verify this probability. The results are shown in Table 2.

In this case the recovered solid was found to be a mixture of unreacted I and triphenylphosphine oxide (V) from a study of its IR spectra ($\nu_{C=O}$ 1615 cm^{-1}, ν_{C-O} 1115 and 1100 cm^{-1}, $\nu_{P=O}$ 1175 cm^{-1}). The ratio of I to V was calculated by means of the intensity ratio of the signals for phenyl protons (τ=2.5) and methyl or methylene protons (τ_{CH_3}=8.92, τ_{CH_2}=6.12). Although V was produced and the yield of ethyl cyclohexaneacetate (III) increased in this reaction, it was obvious that the pyrolysis itself was not accelerated by the addition of the peroxide. V is thought to have been produced by the reaction of the *t*-butoxy radical with triphenylphosphine or with I.

Azobisisobutylonitrile was also used as an addend since it had no oxygen atom which was liable to interact with the phosphorus atom. The temperature of the bath was about 130°C, and a mixed solvent (cyclohexene 2 : benzene 1) was used to dissolve I at room temperature. In this case the decomposition caused by the attack of the radical on I was negligible.

Pyrolysis was carried out in a 100-m*l* autoclave in order to examine the effect of oxygen (Table 2b). The reaction was very fast; the conversion had reached 94% after 8 hr. In this experiment V and III were both obtained in quite good yields. It is reasonable that the yield of V increased in the presence of oxygen, but we cannot explain why the III increased also. Further studies will be necessary to explain the results of the pyrolysis of I in the presence of air.

Now let us compare the results of the pyrolysis

and photolysis of I in cyclohexene. In the case of photolysis, triphenylphosphine was not obtained at all, while diphenylphosphinic acid was obtained on the oxidation of the photolysate with hydrogen peroxide. Benzene was also formed almost quantitatively. The quantum yield of the benzene formation was 0.02. This value was equal to that for the photolysis of triphenylphosphine under the same conditions. Furthermore, the yield of benzene increased linearly with the irradiation time until the conversion reached 20%.[4] From these results, we could reject the possibility that triphenylphosphine was produced by P=C bond fission, followed by photolysis. It is most probable that P-phenyl bond breaks first in photolysis (Eq. (2a)). However, we cannot reject the probability that the electronically-excited triphenylphosphine produced in photolysis decomposes immediately (Eq. (2b)). On the other hand, in the pyrolysis no benzene and phenylcyclohexane were detected at all, while triphenylphosphine was obtained. Consequently, it is obvious that only P=C bond fission occurs, while P-phenyl bond fission does not occur at all, in the pyrolysis (Eq. (1)).

The yield of triphenylphosphine was very low, probably because of its high reactivity to the radicals.

No effect of oxygen was observed in photolysis, whereas in pyrolysis there was a remarkable effect and the decomposition was accelerated enormously.

The rate constants of this pyrolysis were obtained by titrating the unreacted ylid with HCl after the pyrolysis over the temperature range of 160—200°C.[5] The Arrhenius plot of the pyrolysis of I was linear (Fig. 1), and the activation energy of this reaction was calculated to be 28 kcal/mol.

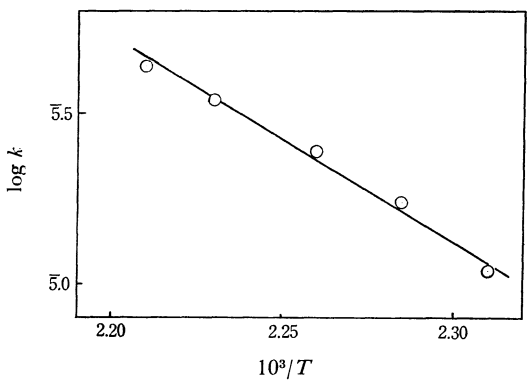
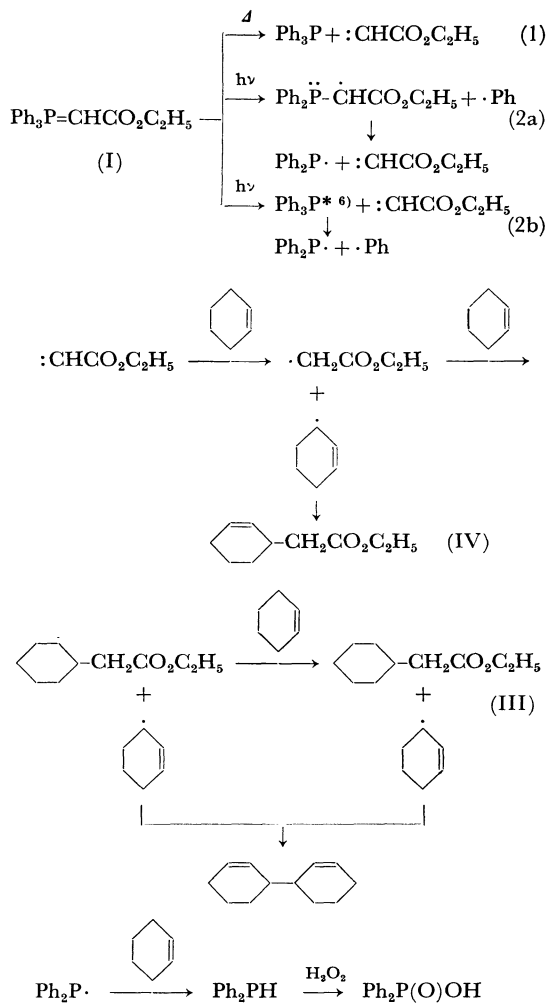


Fig. 1. Arrhenius plot of the pyrolysis.

The probable pyrolysis and photolysis mechanisms are as follows:



Experimental

Pyrolysis in the Pyrex Tube. A solution of I (500 mg, 1.44 mmol) in cyclohexene (15 m*l*) was degassed in a 20-m*l* Pyrex tube (10 mm I.D.) by the usual freeze-and-thaw method. This solution was then heated for 40 hr in an oil bath (at about 180°C). After cooling, the low-boiling material was distilled under reduced pressure. Benzene was not detected in this distillate. By the addition of *n*-hexane to the residue, the unreacted I was removed. The recovered I was 331 mg. 3,3′-Bicyclohexenyl (II), ethyl cyclohexaneacetate (III), and ethyl 2-cyclohexeneacetate (IV) were obtained from the *n*-hexane layer. A quantitative determination of these products were made by glc (Dinonyl phthalate), as has been described in a previous paper.[4] The triphenylphosphine was determined by glc (Thermol-3), using ethyl stealate as the internal standard.

The Isolation of $Ph_2P(O)OH$. The phosphorus-containing compound produced in the photolysis of I was isolated in the following manner.

5) The Ph_3P produced in the pyrolysis was assumed to have scarcely any effect upon the titration because of its small quantity.

6) The asterisked Ph_3P has an excess energy; hence, it decomposes as soon as it is produced.

The photolysed material was oxidized with hydrogen peroxide at pH 12—13, and then extracted with ether. A white precipitate was formed on the acidification of aqueous layer with HCl. This was extracted with ether and then recrystallized from EtOH. The IR spectrum of this material was identical with that of an authentic sample; mp 186—189°C (lit,[7] 191°C).

The Determination of the Activation Energy. After the pyrolysis at 160—200°C, the unreacted I was titrated with HCl, and the rate constants of the decomposition of I were calculated.

7) L. Horner, H. Hoffmann and H. G. Wippel, *Chem. Ber.*, **91**, 64 (1958).