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WAVELENGTH DEPENDENCE IN THE PHOTOLYSIS OF TRIPHENYLPHOSPHINE-DIPHENYLMETHYLENE IN CYCLOHEXENE[1]

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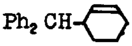
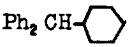
In the previous paper on the photolysis of triphenylphosphine-carbethoxymethylene (I) in cyclohexene[2], we have shown that triphenylphosphine (TPP) is not produced at all and benzene is formed almost quantitatively. We have suggested that P-phenyl bond is broken first in this photolysis. These results greatly differ from those of photolysis of triphenylphosphine-diphenylmethylene (II) in cyclohexene by Tschesche[3], where TPP is formed in 83% yield[4]. In order to clarify the difference in the behavior of these two ylids, more detailed investigation on the photolysis of II in cyclohexene was carried out. We wish to report here that formation of TPP depends on wavelength of exciting light.

$Ph_3P{=}CHCO_2C_2H_5$ (I)

$Ph_3P{=}CPh_2$ (II)



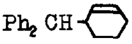
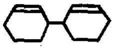
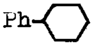
(III)



(IV)

Degassed II (1g) — cyclohexene (40ml) solutions were sealed in quartz or Pyrex tubes and irradiated with a 350W high pressure mercury lamp. After 5 – 7 hr of irradiation, the red color of II had disappeared. 1,1,2,2,-Tetraphenylethane precipitated as a white solid (m.p. 214 – 215°C, recrystallized from EtOH) after removal of low boiling materials. In Pyrex tubes, TPP was produced in 90% yield, while the yield of benzene was only 5%. In quartz tubes, on the other hand, TPP could not be detected at all and benzene was produced in 78% yield. Diphenylcyclohexen-2-yl methane (III) was obtained in fairly good yield in both quartz and Pyrex tubes. Formation of III has not been reported in the previous paper[3]. The structure of III was confirmed by comparison with an authentic sample in glc. Retention times of III and its catalytic hydrogenation product IV were equal to those of an authentic III and IV, respectively. The results are shown in Table I.

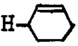
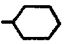
Table I. Photolysis of $Ph_3P{=}CPh_2$ in Cyclohexene

	quartz tube		Pyrex tube		
Product	mg	Yield,%^{*1}	mg	Yield,%	Yield,%^{*3}
PhH	142	78	10	5	-
Ph_2CH_2	24	6	nd^{*2}	-	33
	335	57	330	56	-
$Ph_2CHCHPh_2$	74	10	nd	-	27
Ph_3P	0	0^{*4}	550	90	84
	99	-	nd	-	-
	42	11	nd	-	-

*1) Yield (mole %), based on II used. *2) nd; not determined. *3) See ref. 3. *4) $Ph_2P(O)OH$ was obtained in 18% yield on the oxidation of the photolysate.

In order to make clearer this wavelength dependence and photolysis mechanisms, quantum yield measurements were made in a 40 ml quartz cell using light of three wavelength regions, that is, 253.7 nm, 320-400 nm and 400-500 nm light. Light intensity was determined by ferrioxalate actinometry[5]. The results are presented in Table II. Wavelength dependence on formation of TPP and benzene is remarkable. On irradiation at 253.7 nm, TPP is not produced at all, whereas it is easily produced using light above 300 nm. The yield of benzene at 253.7 nm increased almost linearly with the irradiation time.

Table II. Quantum Yields of the Products[*1]

Product	Wavelength 253.7 nm[*2]	Wavelength 320—400 nm[*3]	Wavelength 400—500 nm[*4]
PhH	0.02	0	0
Ph_2CH_2	0.01	0.06	0.05
Ph_2CH- 	0.007	0.03	0.02
Ph_3P	0	0.01	0.02
	0.004	nd	nd
Ph- 	0.0007	0	0

*1) II: 7×10^{-3} mole/l in cyclohexene. *2) Low pressure mercury lamp. *3) Medium pressure mercury lamp, Toshiba glass filter UV-35 and UV-D25. *4) Medium pressure mercury lamp, Toshiba glass filter UV-39 and $CuSO_4$ aqueous solution.

Further, the quantum yield for benzene formation was equal to that in photolysis of TPP in cyclohexene under the same conditions[2]. It will be less probable that TPP is formed, followed by its photolysis to phenyl and diphenylphosphinyl radicals. Such wavelength dependence was not observed in photolysis of I in cyclohexene.

The UV spectrum of II has a maximum at 432 nm[6]. This absorption would be attributed to a benzhydryl anion[7] or an intramolecular charge transfer structure[8]. In photolysis of II using light above 320 nm, P=C bond will be broken first via an intramolecular charge transfer (1) or by light absorption at a benzhydryl moiety. Thus, TPP is produced. On the other hand, the light energy of 253.7 nm will be absorbed mainly at a triphenylphosphinyl moiety, since the UV spectrum of II in wavelength regions shorter than 300 nm is similar to that of TPP. P-phenyl bond will be broken first in this case in a similar way to photolysis of TPP[2,9].

$$Ph_3P{=}CPh_2 \longleftrightarrow Ph_3\overset{+}{P}{-}\overset{-}{C}Ph_2 \xrightarrow{h\nu} Ph_3\overset{\bullet}{P}{-}\overset{\bullet}{C}Ph_2 \quad (1)$$

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4) This is the product expected from P=C bond fission.

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6) The exact extinction coefficient could not be determined since II was easily oxidized.

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