CHEMISTRY LETTERS, pp. 147-150, 1972. Published by the Chemical Society of Japan

THE PHOTOCHEMICAL AND THERMAL REACTIONS OF DIETHYL PHENYLAZOPHOSPHONATE WITH CYCLOHEXENE

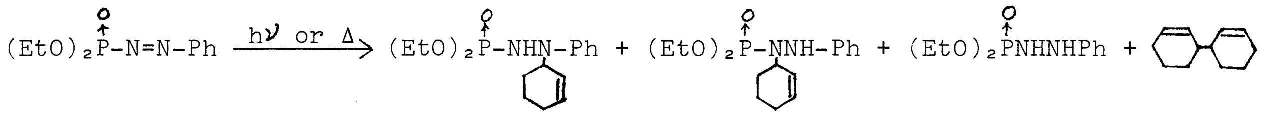
Yoshihiro NAGAO, Kensuke SHIMA, and Hiroshi SAKURAI
The Institute of Scientific and Industrial Research,
Osaka University, Suita, Osaka, Japan

The photochemical and thermal reactions of diethyl phenylazophosphonate with cyclohexene afforded two 1:1 adducts. In the photochemical reaction, there was the wavelength dependence for the formation of the adducts. It was proposed that the active species for the formation of the adducts were different between the thermal and photochemical reactions.

Although there are many papers on the photolysis and thermolysis of azo compounds and the detailed reaction mechanism has been studied, little is known on the photochemical and thermal addition reactions of these compounds to olefins.[1] We obtained two 1:1 adducts on the photochemical and thermal reactions of diethyl phenylazophosphonate (I) with cyclohexene in the course of our studies on the photochemical reactions of organophosphorus compounds,[2] and examined the mechanism of these reactions.

A cyclohexene solution of I (2 g in 80 ml) was irradiated with a high pressure mercury lamp through a Pyrex filter for two days. Removal of the solvent gave a residue which was chromatographed on silica gel to give a mixture of two 1:1 adducts, II and III, while on alumina to give II (mp 81°C) only. Diethyl β-phenylhydrazinophosphonate (IV) and bicyclohexenyl (V) were also obtained.

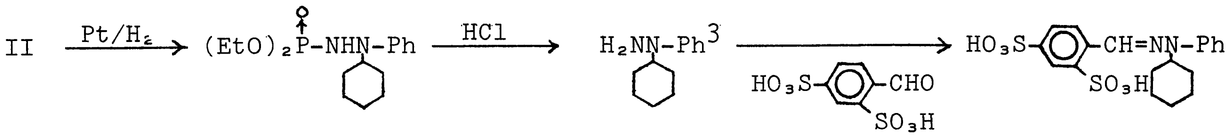
This reaction was effected also by heating a solution of I in cyclohexene (I:500 mg in 4 ml) in a Pyrex tube at about 150°C for two days.

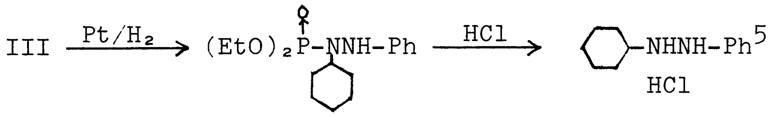


I	II	III	IV	V
Photochemical*	26%	15%	5%	1%
Thermal*	8%	12%	6%	1%

* Yields were determined by glc.

The structure of the adducts was determined by elemental analysis, NMR and mass spectra, and further by the hydrogenation followed by the acid hydrolysis shown in the following scheme.





Both in the photochemical and thermal reactions of I, diethyl phenylphosphonate was not detected at all, and the evolution of nitrogen was not observed.

A noticeable difference in the results of the photochemical and thermal reactions was found in the ratio of the yields of the adducts (III/II). In the photochemical run, the ratio was 0.6. In contrast, it was 1.5 in the thermal run.[6] These results suggest the possibility that the two reactions proceed through different mechanisms. In order to make this point clear, further work has been done.

It was ascertained by measuring the quantum yields that there existed the wavelength dependence for the formation of the adducts. The quantum yields for the formation of the adducts (ϕ_A) and the disappearance of I (ϕ_D) were as follows.[7]

$\phi_A = 2\times10^{-3}$, $\phi_D = 3\times10^{-3}$ (at 366 nm), $\phi_A = 2\times10^{-4}$ (at 313 nm), $\phi_A = 0$ (at 450-550 nm)

As the azophosphonate (I) has a $\pi\pi^*$ maximum at 300 nm and an $n\pi^*$ maximum at 490 nm, the $\pi\pi^*$ excitation was shown to be important for the photochemical reaction. However, the quantum yield at 313 nm was smaller than that at 366 nm. Other reaction such as cis-trans isomerization might occur competitively at this wavelength.[8]

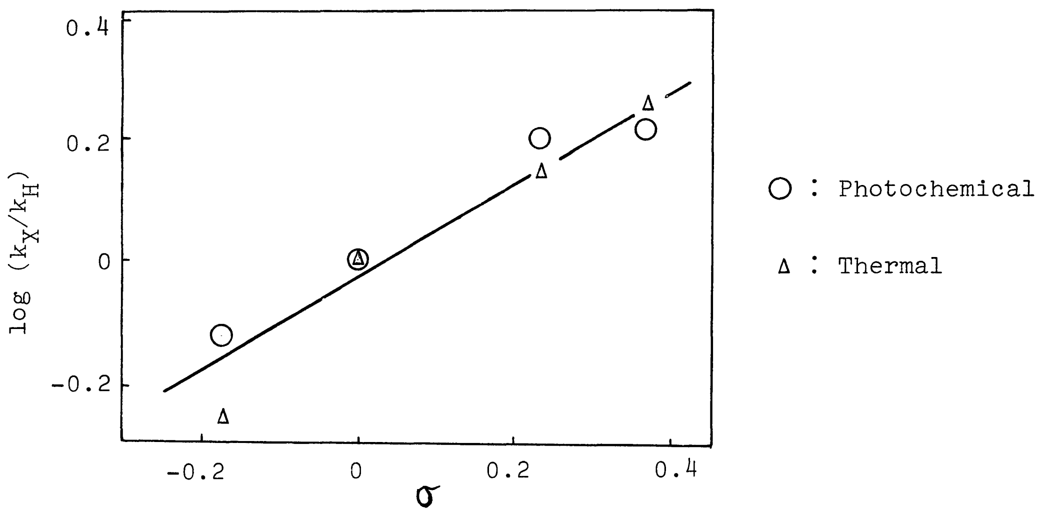
Although diethyl azodicarboxylate (VI) has been reported to give a 1:1 adduct in the photochemical and thermal reactions with cyclohexene, it has not been known whether the wavelength dependence existed or not for the photochemical reaction.[9]

$$EtO_2C\text{-}N{=}N\text{-}CO_2Et \quad (VI)$$

Since the photochemical reaction was found to take place by the absorption of light energy at the phenylazo moiety, we examined the influence of substituents on the phenyl ring on the reactions.[10] Hammett plots of the relative rate for the formation of the adducts vs. σ gave linear correlations both in the photochemical and thermal reactions. Positive ρ values showed the reactions to be electrophilic.

Substituent on the Phenyl Ring (X)	Photochemical		Thermal	
	III/II	k_X/k_H	III/II	k_X/k_H
p-Me	0.75	0.76	2.2	0.58
H	0.66	1.0	1.4	1.0
p-Cl	0.82	1.6	2.2	1.44
m-Cl	0.64	1.7	1.8	1.88
o-Cl	1.4	2.6	2.9	3.79

Hammett Plot for the Reaction of I with Cyclohexene

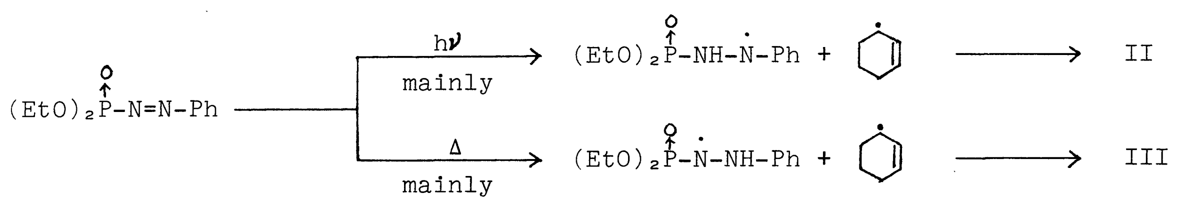


Although similar ρ values were obtained for the photochemical and thermal reactions, no detailed discussion could be done since reliable data have not been available on the effect of substituents on the phenyl ring in an excited molecule.

It is clear that the ratios (III/II) are quite different between the thermal and photochemical reactions for all substituents except for o-Cl.^{11}

As the adducts were confirmed to be stable and not to isomerize each other under the conditions employed in the reactions and determination by control experiments, it seemed most reasonable to assume that the differences in the ratios resulted from the difference in the nature of the active species in the two systems. This result is interesting, since a common active species has been proposed to exist both in the photochemical and thermal reactions of VI with cyclohexene.^{9}

As the present reactions were supposed to proceed through a radical mechanism on the basis of the isolation of V, and furthermore shown to be electrophilic, we interpret the differences of the ratios as follows. In the thermal reactions, phosphoryl group may raise the electrophilicity of the azo nitrogen atom which is more remote from the phosphoryl group. Hence, the yield of III may be increased. On the other hand, in the photochemical reactions, an excited azophosphonate is produced by the absorption of the light energy of 313 nm or 366 nm at the phenylazo moiety. This excited species may abstract a hydrogen atom from cyclohexene more efficiently at the azo nitrogen atom which is more remote from the phenyl group because of the electron attractive effect of a phenyl group in the $\pi\pi^*$ state. The yield of II may be increased in this case. These consideration can be formulated as follows.



The possibility that either reaction proceeds through an addition-abstraction mechanism cannot be excluded thoroughly by these experiments. Further work is now under way.

References

1) A. A. Lamola and N. J. Turro, "Energy Transfer and Organic Photochemistry," p 262, Interscience Publishers, New York, N. Y. (1969).

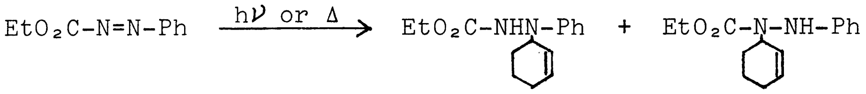
2) Y. Nagao, K. Shima and H. Sakurai, Kogyo Kagaku Zasshi, 72, 236 (1969); Bull. Chem. Soc. Japan, 43, 1885 (1970); Tetrahedron Lett., 2221 (1970) and 1101 (1971).

3) Identified by comparison with an authentic sample by glc.

4) Identified by comparison with an authentic sample by tlc.

5) Isolated as white crystals and identified by comparison of the IR spectrum with that of an authentic sample. Mixed mp 189°C.

6) We isolated two analogous adducts by the thermal and photochemical reactions of ethyl phenylazocarboxylate (VII) with cyclohexene. The ratios IX/VIII were different between the photochemical and thermal runs in a similar manner as I. IX/VIII : 0.9 (photochemical), 1.7 (thermal).
The reaction rate of I with cyclohexene was much faster than that of VII.



VII VIII IX

7) Quantum yields were determined at 0.025 M concentration of I using a potassium ferrioxalate actinometer.

8) The $n\pi^*$ absorption band was increased and its maximum was shifted to shorter wavelength with the irradiation time in the UV spectrum.

9) A. G. Ahlgren, A. B. Akermark and K. I. Dahlquist, Acta Chem. Scand., 22, 1129 (1969).

10) In the kinetic experiments, cyclohexene solutions of I (4 mmol in 3 ml) in Pyrex tubes were degassed by the usual freeze and thaw method and irradiated with a high pressure mercury lamp or heated in an oil bath (at about 130°C). The conversion of the starting material was limited within 20%. The yields of the adducts were determined by glc (SE-30, 1 m, 190°C).

11) It should be due to the steric hindrance of an ortho chlorine atom that the yields of II were poorer than those of III both in the photochemical and thermal runs.

(Received October 15, 1971)