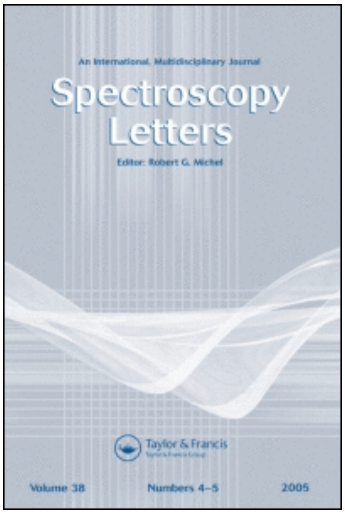

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Photolysis and E. S. R. Studies on Triphenylphosphinecarbethoxymethylene

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To cite this Article Zanger, M. and Poupko, R.(1977) 'Photolysis and E. S. R. Studies on Triphenylphosphinecarbethoxymethylene', Spectroscopy Letters, 10: 9, 737 — 745
To link to this Article: DOI: 10.1080/00387017708065007
URL: http://dx.doi.org/10.1080/00387017708065007

SPECTROSCOPY LETTERS, 10(9), 737-745 (1977)

PHOTOLYSIS AND E.S.R. STUDIES ON TRIPHENYLPHOSPHINECARBETHOXYMETHYLENE

Keywords: E.S.R., photolysis, phosphorus ylides

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Although several different groups have studied the photolysis of phosphorus ylides, none have utilized e.s.r. to support the postulated decomposition mechanisms. The fundamental question which awaits a definitive answer is which bond breaks first upon photolysis. Tschesche[1] and de Silva[2] utilizing the ylides (1) and (2) suggested that the carbon-phosphorus double bond was initially broken while Nagao[3] using (3) proposed phenyl-phosphorus bond cleavage.

(1) $Ph_3P{=}CPh_2$ (2) $Ph_3P{=}CHCOPh$ (3) $Ph_3P{=}CHCO_2C_2H_5$

After reviewing Tschesche's work, however, Nagao modified his hypothesis and stated that the decomposition was wavelength dependent; that below 3000Å, the phenyl-phosphorus bond broke while at longer wavelengths it is the carbon-phosphorus double bond which cleaved. A condensed mechanistic scheme is shown in equations (1 & 2). Since all of the proposed mechanisms were based only upon the analyses of the photolysis products, it seemed worthwhile to investigate this process using e.s.r. to observe and identify any transient radicals.

1. (a) $Ph_3P{=}CHCO_2C_2H_5 \xrightarrow{h\nu(<3000\text{Å})} Ph_2\dot{P}{=}CHCO_2C_2H_5 + Ph\cdot$

   (b) $Ph_2\dot{P}{=}CHCO_2C_2H_5 \longrightarrow Ph_2\dot{P} + :CHCO_2C_2H_5$

2. $Ph_3P{=}CHCO_2C_2H_5 \xrightarrow{h\nu(>3000\text{Å})} Ph_3P + :CHCO_2C_2H_5$

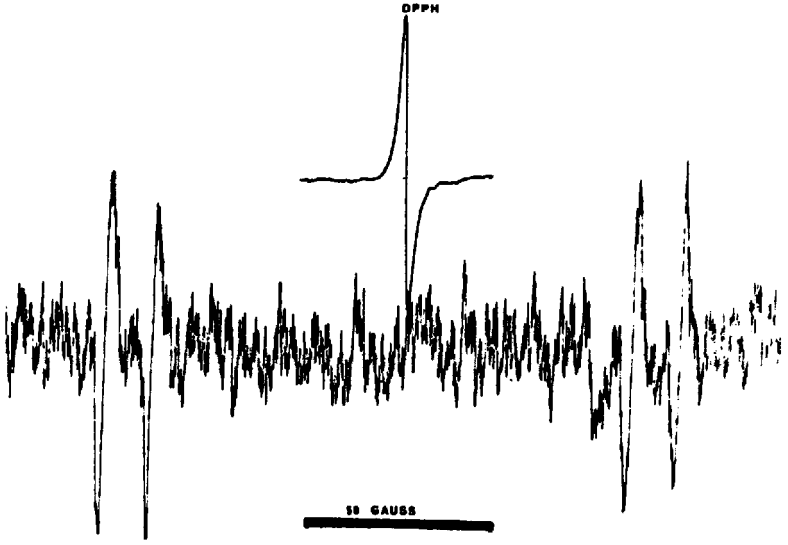
Samples of (3) in benzene were photolyzed using an OSRAM 200-W high pressure mercury lamp housed in a Wild reflector. The samples were run in quartz tubes in the cavity of a Varian E3 e.s.r. spectrometer. At ambient temperature, a weak doublet of doublets was observed (Spectrum I). This spectrum was assigned the structure (4) with a_P = 150 G and a_H = 14 G; g = 2.0037.

(4) $Ph_2\dot{P}=CHCO_2C_2H_5 \longleftrightarrow Ph_2P-\dot{C}HCO_2C_2H_5$

(5) $Ph_2P\cdot$

This radical was postulated by Nagao as the primary one arising from photolysis below 3000Å. The signal disappeared immediately when irradiation was stopped. Many variations in procedure did not lead to significant increases in the intensity of this very weak signal. On cooling the sample, no changes in the spectrum were observed until the freezing point of the solvent was reached, then the two doublets disappeared to be replaced with a broad signal with a g-value of 2.0031. When the temperature sequence was reversed, both species could be observed during the thawing period of the solvent.

In order to identify the radical produced in the solid phase, triphenylphosphine was irradiated under conditions similar to those already described. At temperatures above the freezing point of the solvent, no signals were produced. However, in the temperature range -197° to -90°, a virtually identical broad signal to that given by (3) was observed; g = 2.0034. This species was quite stable at low temperature. The radical formed from triphenyl-



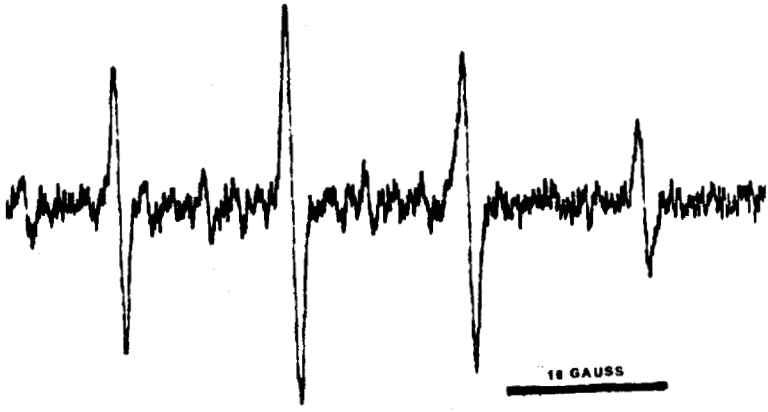
Spectrum I

phosphine and (3) at low temperature is most probably diphenylphosphino (5). There are numerous reports of the production of this species[4] in the photolysis of phosphines and related compounds. The reported g-value for diphenylphosphino is 2.0036 $\pm$ 0.0005[5].

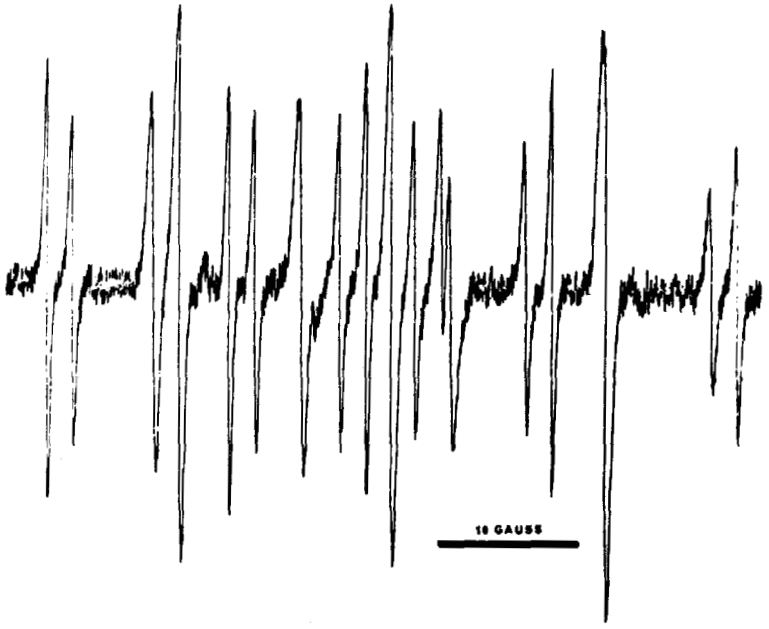
Further experiments to positively identify the radicals (4) and (5) were carried out by using the spin trap, t-nitrosobutane. When (3) and the spin trap were irradiated with full intensity u.v. light, a complex spectrum, obviously consisting of more than

one species, was observed. However, on irradiation at room temperature, with a greatly attenuated u.v. source, a single quartet was produced (Spectrum II). This signal is attributed to the trapped diphenylphosphino radical (6): a_N=10.7G, a_P=11.5G. When the u.v. illumination was increased either in intensity or duration, a strong new signal was superimposed on the original quartet, which consisted of twelve lines (Spectrum III).

The constants for this radical are a_N=13.5G, a_P=21.8G, a_H=1.9G and it is ascribed to (7), the spin-trapped radical (4). In addition to radicals (6) and (7), a third radical arising from the decomposition of the



Spectrum II



Spectrum III

spin trap was also observed. The di-t-butyl nitroxide radical gave a triplet with a_N=15.8G[7].

(6) $Ph_2P(O\cdot)-N-t\text{-}bu$

(7) $Ph_2P(O\cdot)-CH(CO_2C_2H_5)-N-t\text{-}Bu$

Similar experiments were performed with triphenylphosphine and the spin trap. Photolysis at room temperature gave two analyzable signals, the spin trap decomposition radical, a_N=15.6G and the trapped

diphenylphosphinyl (6); a_N=10.5, a_P=11.8G. A third signal, a triplet with a_N=11.5G could not be assigned.

From the results obtained it seems apparent that the first radical which is formed is diphenylphosphino (5). This species arises from triphenylphosphine, so that even at wavelengths below 3000Å, it must be the carbon-phosphorus double bond which cleaves first. Nagao's suggestion that (4) is the primary radical formed is not supported by either the variable temperature experiments or those utilizing a spin trap. Species (4) then is most likely formed by a recombination of the diphenylphosphino radical with carbethoxymethylene. This postulate gains support from the observation that (4) disappears in the solid phase (recombination is impossible) and also because it forms in very low yield. The proposed reaction mechanism for the photolysis is summarized in the following scheme, (equations 3, 4 & 5):

3. $Ph_3P{=}CHCO_2C_2H_5 \xrightarrow{h\nu} Ph_3P + :CHCO_2C_2H_5$

4. $Ph_3P \xrightarrow{h\nu} Ph_2P\cdot + Ph\cdot$

5. $Ph_2P\cdot + :CHCO_2C_2H_5 \longrightarrow Ph_2\dot{P}{=}CHCO_2C_2H_5$

Step (3) can occur at long wavelengths while step (4) requires light of higher energy (e.g. <3000Å). There is no indication, however, that phenyl-phosphorus bond cleavage ever occurs in the parent compound.

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Received: 6-8-77
Accepted: 6-28-77