MECHANISTIC STUDY ON THE IRRADIATION OF IMINOPHOSPHORANES

by

ANDREW SUET-WAI YIM

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Name: Andrew Suet-Wai Yim

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Examining Committee:

A. C. Oehlschlager
Senior Supervisor

E. Kiehlmann
Examining Committee

L. K. Peterson
Examining Committee

K. N. Slessor
Examining Committee

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Title of Thesis/Project/Extended Essay

MECHANISTIC STUDY ON THE

IRRADIATION OF IMINOPHOSPHORANES

Author:

(signature)

ANDREW S. YIM

(name)

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(date)

ABSTRACT

The photodissociation of N-aryl- and N-alkyl-triphenyliminophosphoranes (ylids) lead to triphenylphosphine and products which could be considered to be derived from monovalent nitrogen (nitrene) intermediates. Only one case of the irradiation of a triphenyliminophosphorane has been reported (H.Zimmer and M. Jayawant, Tetra. Letters, 5061 (1966)).

Like the irradiation of methylenetriphenylphosphoranes, the irradiation of N-substituted triphenyliminophosphoranes is also wavelength-dependent, resulting in different modes of photodecomposition.

Ylids with resonance-stabilizing substituents on the nitrogen are stable to irradiation with a pyrex filter ($>$300 nm) but liberate benzene when irradiated in a quartz cell ($>$200 nm).

N-aryl ylids afford photoexcited ylids upon irradiation, resulting in azobenzene derivatives and triphenylphosphine. Aryl nitrenes are unlikely intermediates. In the presence of oxygen, photooxidation takes place to produce triphenylphosphine oxide and secondary products. Aryl nitrenes are apparently involved via deoxygenation of nitrosobenzene derivatives by triphenylphosphine. Both of the latter are products of the irradiation.

N-alkyl ylids may generate alkyl nitrenes upon irradiation, although more concrete evidence is necessary to clarify this.

A proposal is made for further research in this study.

TO MY WIFE AND CHILDREN

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INTRODUCTION

Molecules possessing double bonds between pentavalent phosphorus and carbon (methylenephosphoranes) or nitrogen (iminophosphoranes, monophosphazenes, or phosphinimines) (I-1) are classified as ylids.[1]

$$R_3P{=}X \longleftrightarrow R_3\overset{+}{P}{-}\overset{-}{X}$$

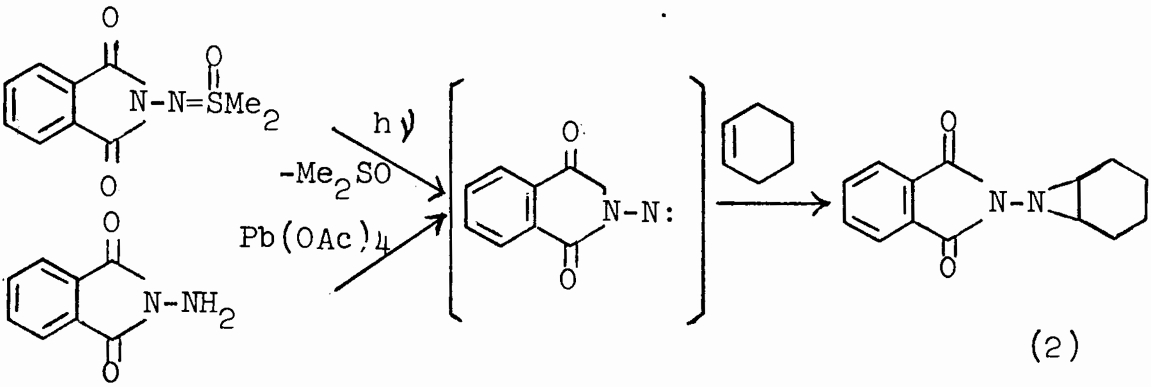
(I-1), $X = CR_2$, NR

Depending on the phosphorus, carbon and nitrogen substituents, some of these ylids are susceptible to photolytic fragmentation. Radiation induced homolytic dissociation of the heteromultiple bonds of these ylids may lead to a phosphine (I-2), and a reactive carbene or nitrene (I-3) (equation 1).

$$R_3P{=}X \xrightarrow{h\nu} \underset{(I\text{-}2)}{R_3P:} + \underset{(I\text{-}3)}{:X} \qquad (1)$$

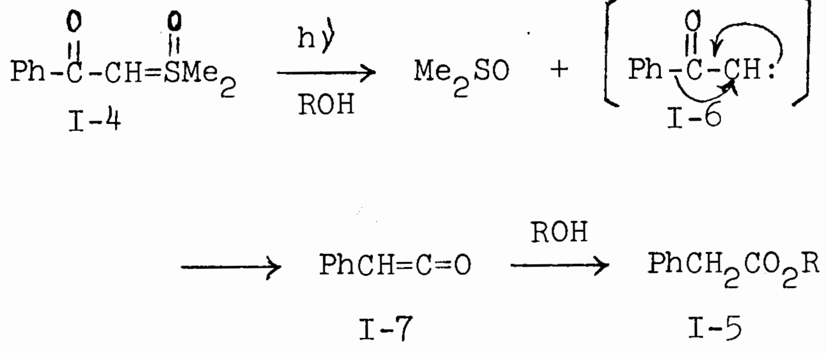
$X = CR_2$, NR

Amino nitrenes have been invoked in a number of nitrogen-sulfur ylid photodissociations. Anderson and co-workers[2] irradiated a number of dimethylsulfoximines in the presence of olefins, and found that aziridines were formed along with dimethylsulfoxide (equation 2). Since the same aziridines were formed when the analogous cyclic N-amino compound was oxidized by lead tetraacetate in the presence of olefins, the amino nitrene was considered the most likely intermediate in both reactions. Strength is lent to this suggestion by several additional reports of the trapping of presumed aminonitrenes with olefins to form aziridines[3]. All of the reactions reported to date that appear to involve trappable amino nitrenes are those where the amino nitrogen is substituted with electron-withdrawing groups.



(2)

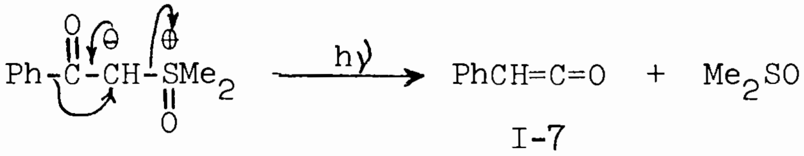
Carbenes have been invoked in a number of carbon sulfur photodissociation reactions. Corey and Chaykovsky[4] first reported the results of irradiation of dimethylsulfoxonium phenacylide (I-4). Upon irradiation in alcohol, the ylid was transformed smoothly to dimethylsulfoxide and the corresponding ester I-5 by a reaction that was envisioned to involve the ketocarbene (I-6) and ketene (I-7) intermediates (equation 3).



$$\underset{\text{I-4}}{\text{Ph}-\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{CH}=\overset{\text{O}}{\overset{\|}{\text{S}}}\text{Me}_2} \xrightarrow[\text{ROH}]{h\nu} \text{Me}_2\text{SO} + \left[\underset{\text{I-6}}{\text{Ph}-\overset{\text{O}}{\overset{\|}{\text{C}}}-\text{CH}:}\right]$$

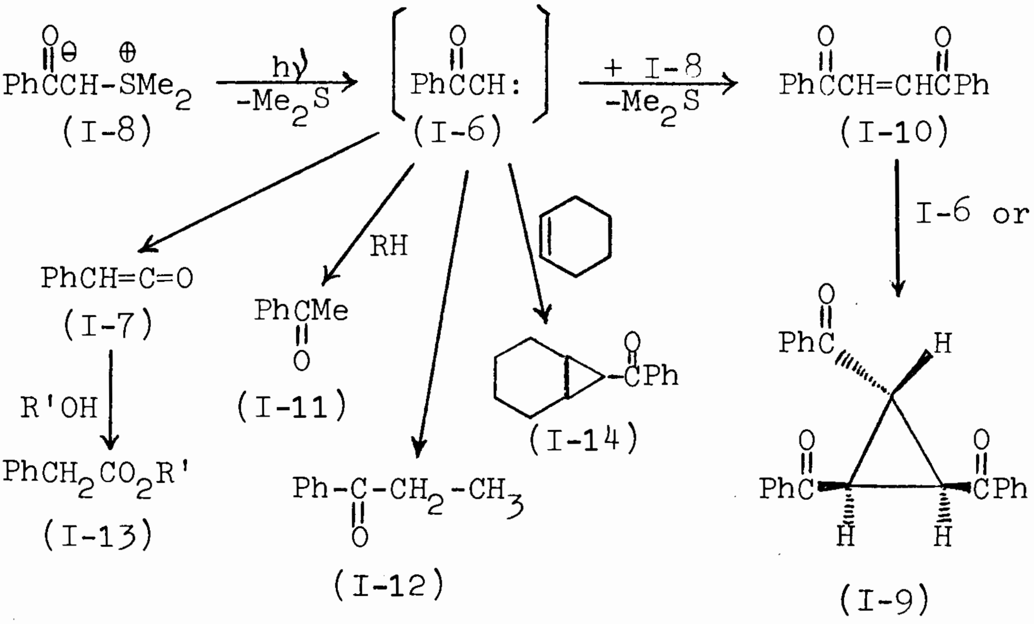
$$\longrightarrow \underset{\text{I-7}}{\text{PhCH=C=O}} \xrightarrow{\text{ROH}} \underset{\text{I-5}}{\text{PhCH}_2\text{CO}_2\text{R}} \qquad (3)$$

It was not determined if the formation of the ketene was concerted or involved the ketocarbene intermediate (equation 4).



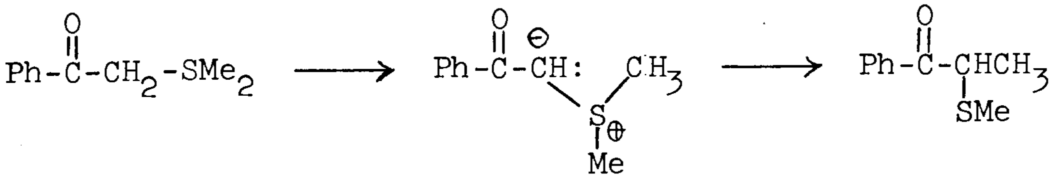
$$\mathrm{Ph{-}\overset{O}{\overset{\|}{C}}{-}\overset{\ominus}{C}H{-}\overset{\oplus}{\underset{\underset{O}{\|}}{S}}Me_2} \xrightarrow{h\nu} \underset{\mathrm{I\text{-}7}}{\mathrm{PhCH{=}C{=}O}} + \mathrm{Me_2SO} \qquad (4)$$

Trost has irradiated dimethylsulfonium phenacylide (I-8) in chloroform and benzene[5], and obtained nearly quantitative yields of trans-1,2,3-tribenzoylcyclopropane (I-9). The cyclopropane (I-9) was envisioned as arising from the reactions of a carbene (I-6) with a second mole of ylid (I-8) to produce dibenzoylethylene (I-10) which subsequently combined either with ylid or carbene to form cyclopropane I-9 (equation 5).



(5)

In ethanol a 48% yield of acetophenone (I-11), propiophenone (I-12), and ethylphenyl acetate (I-13, R' = Et) were formed and the yield of cyclopropane I-9 was lowered to 40-50%. A reasonable mechanistic pathway for the formation of propiophenone involves a Stevens rearrangement of the ylid followed by the photolytic decomposition of the resultant α-methylthiopropiophenone[6]. The ylid does not undergo the Stevens rearrangement thermally under these conditions. This formation of propiophenone was thus taken by the author as an example for the first photolytic induced Stevens rearrangement (equation 6).



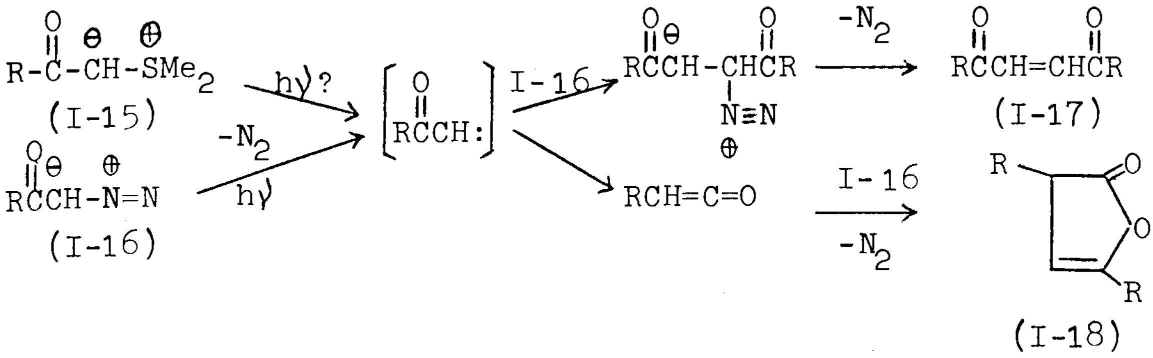
(6)

Using 2-propanol caused significant increase in the ratio of acetophenone to phenylacetic ester. This was considered to indicate that the ketone arose via a carbene intermediate, since an increase in the reactivity of the solvent toward hydrogen abstraction should increase the relative amount of ketone by this route. The formation of benzoylnorcarane (I-14) when the reaction was carried out in the presence of cyclohexene was considered to be another indication of a carbene.

Although the course of reaction can be explained by other mechanisms, they were considered less likely. The ylid I-6 could give a diradical which dimerized to form dibenzoylethylene (I-10) and then underwent further reaction with the irradiated ylid to yield cyclopropane I-9. Photoexcited ylid could react with cyclohexene to form benzoylnorcarane (I-14) or undergo concerted rearrangement to give the ketene I-7 and thus ester I-13. Photoexcited ylid or its diradical could abstract hydrogen from solvent before the cleavage to form ketone I-11.

Recent reports of the photodissociation of carbon-sulfur ylids indicated that a carbene may not be involved in such processes. Serratosa and Quintana[7] reported the irradiation of structurally analogous β-ketosulfonium ylids (I-15) and α-diazoketones (I-16). Since α-diazoketones (I-16) have been shown to produce carbenes upon irradiation the failure of analogous β-ketosulfonium ylids to yield identical products upon irradiation was interpreted to mean that a carbene was not involved in the latter process. Irradiation of ketosulfonium ylids was shown to produce nearly quantitative yields[8,9] of trans-1,2,3-triacylcyclopropanes whereas α-diazoketones (I-16) gave 1,2-diacylethylenes (I-17) and butenolides (I-18) as the main products (equation 7).

Fish and co-workers irradiated 2-methyl-isothiochroman-4-one-3-ylid (I-19) in both chloroform and anhydrous methanol[10] and obtained indan-1-one (I-20) as the only volatile product (equation 8). The absence of methyl ester and methyl ketones indicates a carbene is not involved.



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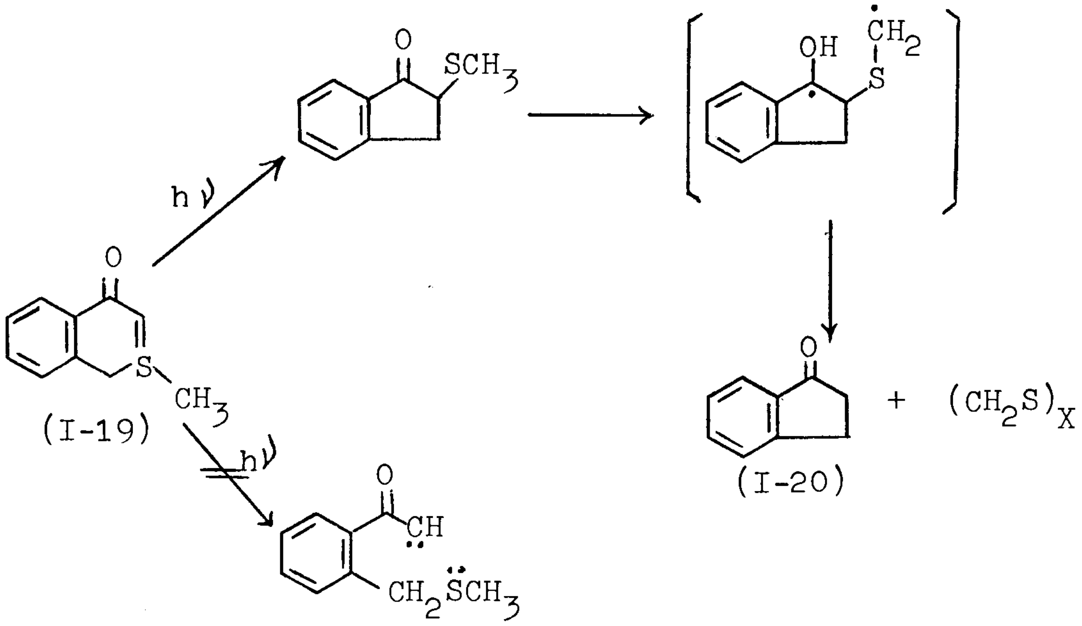
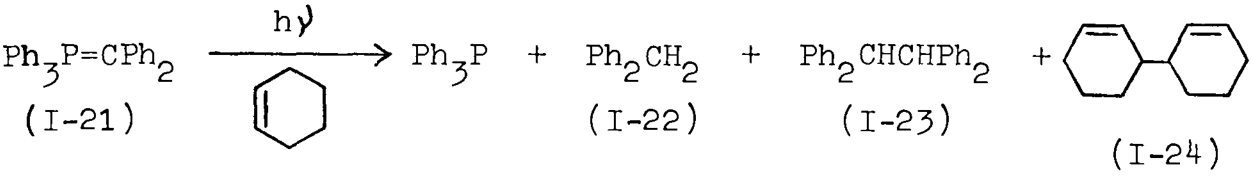


(8)

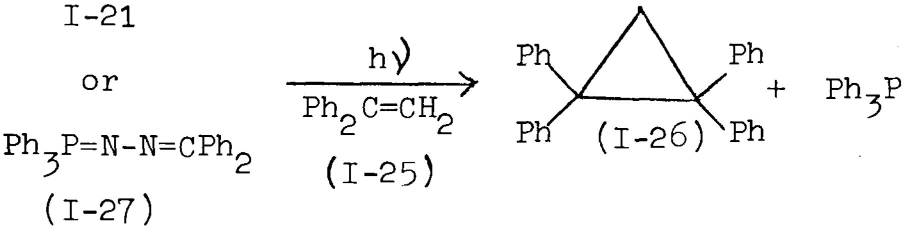
Only a few examples of irradiation of phosphorus-carbon ylids have been reported. Tschesche[11] reported the irradiation of diphenylmethylenetriphenylphosphorane (I-21) in cyclohexene gave triphenylphosphine, diphenylmethane (I-22), 1,1,2,2-

tetraphenylethane (I-23), and 3,3'-bicyclohexenyl (I-24) (equation 9). The formation of these products can be explained by both carbene and photoexcited ylid intermediates, although the former was proposed by the investigator.



(9)

Irradiation of ylid I-21 in 1,1-diphenylethylene (I-23) was shown by Ritter and Kim[12] to yield (73%) 1,1,2,2-tetraphenylcyclopropane (I-26) and triphenylphosphine (equation 10). Irradiation[12] of diphenyltriphenylphosphinazine (I-27) under identical reaction conditions gave cyclopropane I-26, triphenylphosphine, and nitrogen (equation 10).



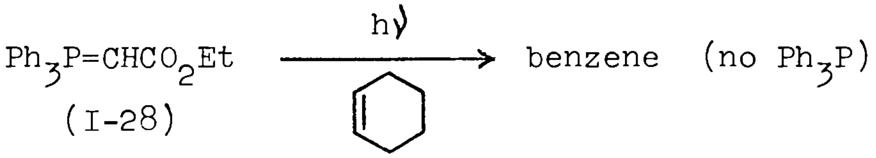
(10)

Diphenylcarbene is a plausible intermediate in these reactions, but based on the fact that ylids are more nucleophilic than carbenes[7], it is probable that phosphinazine, I-27, decomposed upon irradiation to nitrogen and ylid I-21, which reacted with olefin I-25 to produce I-26 (equation 11).

$$(I\text{-}27) \xrightarrow{h\nu} N_2 + \left[Ph_3\overset{\oplus}{P}-\overset{\ominus}{C}Ph_2\right]^* \xrightarrow{(I\text{-}25)} (I\text{-}26) + Ph_3P \qquad (11)$$

Diphenyldiazomethane has been postulated to undergo photodissociation via a carbene. Since comparison of products of phosphinazine I-27 and diphenyldiazomethane under a variety of reaction conditions[13] revealed different product distributions from these two potential carbene sources (Table I), it was considered unlikely that ylid I-27 yielded the same intermediate.

Irradiation of ylid (I-28) in cyclohexene[14] has been reported to produce benzene almost quantitatively but no triphenylphosphine was detected. The benzene was considered to be derived from phosphorus-phenyl bond cleavage of either the ylid or triphenylphosphine.



$$Ph_3P{=}CHCO_2Et \xrightarrow{h\nu} \text{benzene} \quad (\text{no } Ph_3P) \qquad (12)$$

(I-28)

In view of the difference in reported behavior between ylid I-28 and ylid I-21, the irradiation of ylid I-21 in cyclohexene was investigated in greater detail. The formation of triphenylphosphine from this ylid was found to depend on the excitation wavelength (Table II). Such wavelength dependence was not observed in the irradiation of ylid I-28 in cyclohexene.

The UV spectrum of ylid I-21 exhibits a maximum at 432 nm which could be attributed to a benzhydryl anion or an intramolecular charge transfer structure[16]. It was suggested that irradiation of I-21 using light above 320 nm broke the P=C bond via intramolecular charge transfer.

TABLE I

SOLVENT EFFECT ON THE PRODUCT DISTRIBUTION OF THE IRRADIATION OF I-27 AND DIPHENYLDIAZOMETHANE[13]

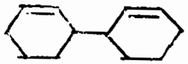
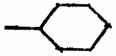
(% YIELD)

COMPOUND	SOLVENTS	$Ph_2C{=}CPh_2$	$Ph_2CHCHPh_2$	$Ph_2C{=}N{-}N{=}CPh_2$	$Ph_2CHOCHPh_2$	Ph_2CO	Ph_3P	Ph_3PO
I-27	BENZENE	2	5	5	2	5	30	50
	DECALIN	5	25	2	2	2	20	50
DIPHENYL-DIAZO-METHANE	BENZENE	2	2	90	5	2	-	-
	DECALIN	2	70	20	5	2	-	-

TABLE II

WAVELENGTH DEPENDENCE OF THE IRRADIATION OF YLID I-21 IN CYCLOHEXENE

(5-7 HOURS)[17]

$Ph_3P=CPh_2$ (I-21)	QUARTZ (200 nm)	PYREX (300 nm)	
benzene	78%[*]	5%	-
Ph_2CH_2	6%	-	33%[***]
Ph_2CH- 	57%	56%	-
$Ph_2CHCHPh_2$	10%	-	27%[***]
Ph_3P	0%[**]	90%	84%[***]
	55%	-	-
Ph 	11%	-	-

[*] % yield calculation based on % theorectical fragment from ylid (mole %)

[**] $Ph_2P(O)OH$ was obtained in 18% yield on oxidation of photolysate.

[***] Result from reference 14.

(equation 13), or light absorption at a benzhydryl moiety. On the other hand, since the UV spectra of ylid I-21 and triphenylphosphine in wavelength regions shorter than 300 nm are very similar[17], light energy of 253.7nm would be expected to break a phosphorus-phenyl bond in a similar manner to that caused by irradiation of triphenylphosphine[14,18,19].

$$\underset{(I\text{-}21)}{Ph_3P{=}CPh_2} \longrightarrow Ph_3\overset{+}{P} - \overset{-}{C}Ph_2 \xrightarrow{h\nu} Ph_3\overset{\bullet}{P} - \overset{\bullet}{C}Ph_2 \qquad (13)$$

Wavelength-dependent irradiation of ylid (I-29) in a number of solvents (Table III), provided evidence that the photoexcited ylid (diradical) I-29a was the reactive intermediate (Figure 1)[20].

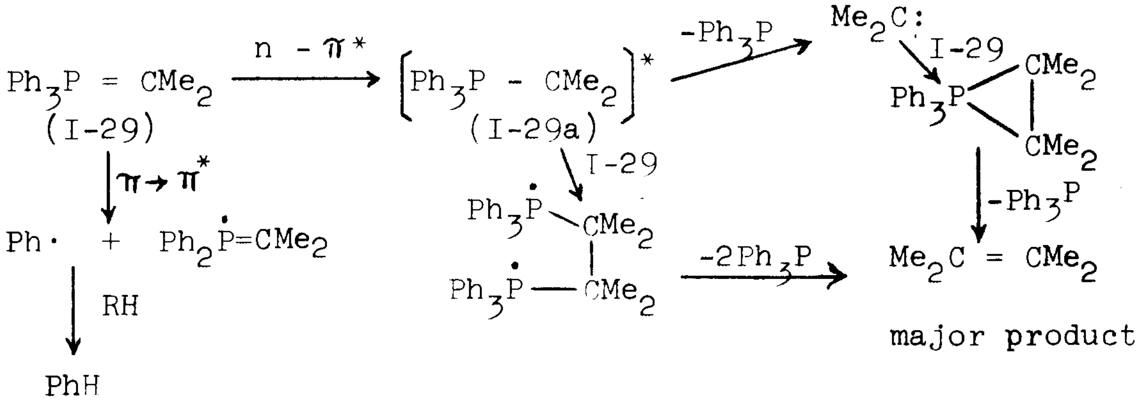


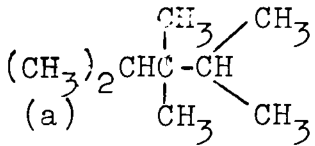
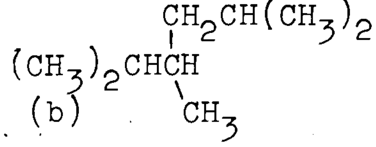
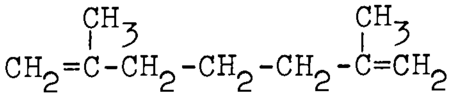
FIGURE 1

Although the behavior of phosphorus-nitrogen ylids at high temperatures has been the subject of some investigation[21], little is known about their photochemical reactions[1].

Zimmer and Jayawant[22] have studied the irradiation of N-t-butyltriphenyliminophosphorane (I-30) in cyclohexene.

TABLE III

IRRADIATION OF $Ph_3P=C(CH_3)_2$ (I-29)[24]

IRRADIATION WAVELENGTH (nm)	SOLVENTS	PRODUCTS (% YIELD)				
		PhH	$(CH_3)_2C=C(CH_3)_2$	$CH_3CH=CH_2$	$(CH_3)_2CHCH(CH_3)_2$	 (a)  (b)
270-290	cyclohexane	59%	39%	1.8%	0.02%	-
270-190 with Triphenylene*	cyclohexane	58%	40%	2.4%	0.02%	-
270-290	$(CH_3)_2CHCH(CH_3)_2$	39%	59%	1.6%	-	a + b 0.5%
290	Isobutane	24%	74%	2.8%	0.02%	 $CH_2=C(CH_3)-CH_2-CH_2-CH_2-C(CH_3)=CH_2$ 0.1%
350	cyclohexane	23%	74%	3.2%	0.02%	-
350	$(CH_3)_2CHCH(CH_3)_2$	17%	79%	2.8%	-	a + b <0.2%

* photo-sensitizer

They observed the formation of triphenylphosphine, triphenylphosphine oxide, t-butylamine (I-31), di-t-butylamine (I-32), t-butylcyclohexenylamine (I-33), 3-3'-bicyclohexenyl (I-24), benzene, nitrogen and hydrogen (Figure 2), which they accounted for by postulating both phosphorus-nitrogen and carbon-nitrogen bond breakage according to Figure 2.

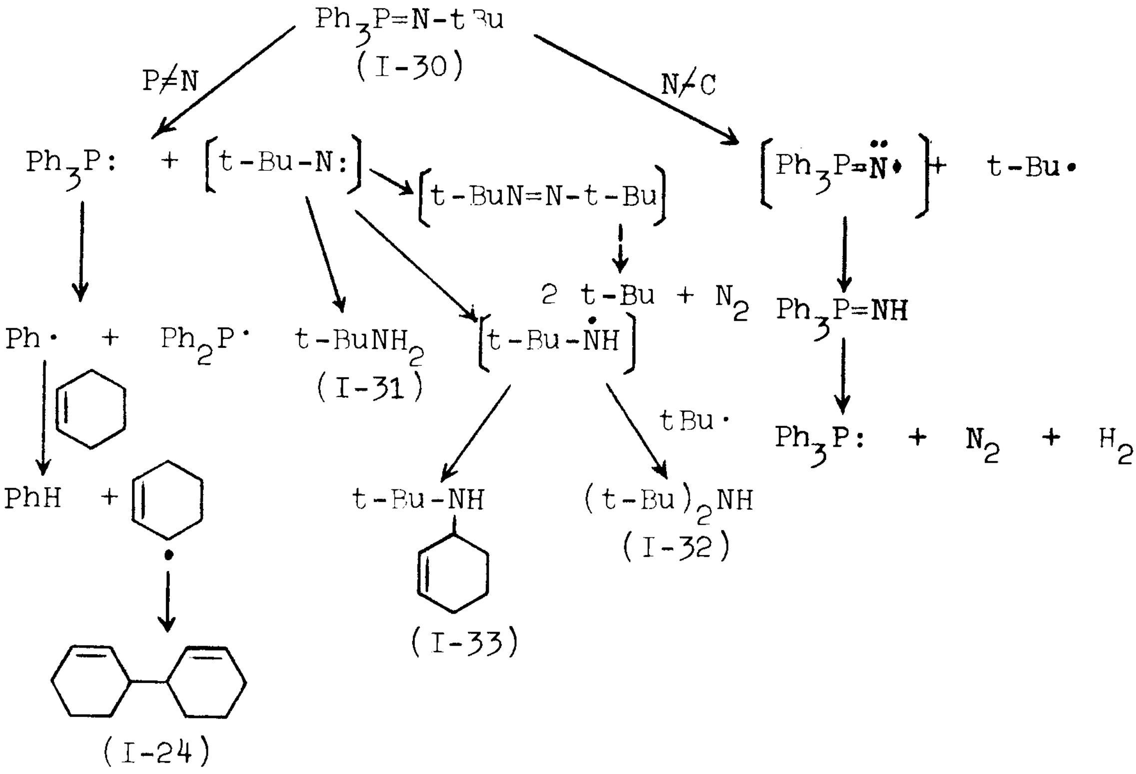


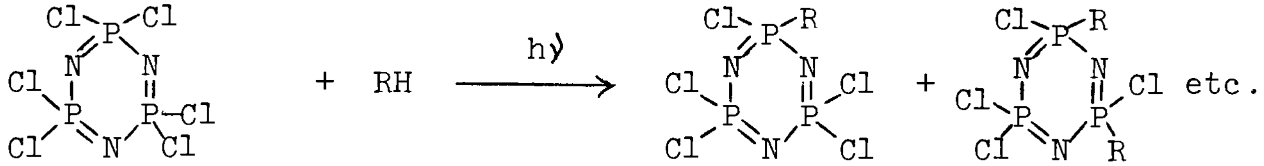
FIGURE 2

From the above mechanism one would expect products which were not observed, e.g. those shown in equation 14.

Films of solid polyiminophosphoranes $(NPCl_2)_3$ or $(NPCl_2)_4$ are unaffected after 40 hours of irradiation by a mercury arc, but solutions of these compounds in hexane,

$$\begin{aligned} \mathrm{tBu}\cdot &\xrightarrow{+\mathrm{H}\cdot} \mathrm{tBuH} \\ \mathrm{tBu}\cdot &\xrightarrow{-\mathrm{H}\cdot} \mathrm{CH_2 = C(CH_3)_2} \\ 2\ \mathrm{tBu}\cdot &\longrightarrow \mathrm{tBu - tBu} \end{aligned} \tag{14}$$

benzene, toluene or decalin do undergo reaction[23] to form brown, gelatinous materials on the walls of the quartz reaction vessel, together with distillable liquids which are organic-substituted cycloiminophosphoranes, possibly formed by the process in equation 15. The photo-stability of the cycloiminophosphoranes to UV irradiation is noteworthy since UV-visible spectroscopic analysis reveals extensive π-electron interactions in these and polyiminophosphoranes[24,25].



(15)

In view of the extensive work carried out of the generation of nitrenes from various precursors and the presumed generation of carbenes from irradiation of analogous phosphorus-carbon ylids, we envisioned that iminophosphoranes would be likely precursors of nitrenes.

Our prime objective in this study was to investigate the mechanism involved in and the effect of nitrogen and phosphorus substitution on the course of photodissociation of iminophosphoranes. Since photodecomposition of iminophosphoranes with various substituents on the nitrogen was observed to occur, we sought to determine if a nitrene or excited ylids were the reactive intermediates.

We also endeavored to determine if electron-withdrawing or resonance-stabilizing substituents on nitrogen would reduce the phosphorus-nitrogen double bond character making it photostable.

If nitrenes were indeed produced during the irradiation of triaryliminophosphoranes, it would provide an alternative means of generating nitrenes[26] under relatively mild conditions compared with reduction of nitro-[27] and aryl-nitroso compounds[28], and oxidation of N-amino compounds[2,29].

Since azides have served as nitrene precursors, we chose to compare the course of photodissociation of iminophosphoranes with that of structurally related azides. The comparison is not completely straightforward since azides react by two principal mechanisms with their preferred substrates, olefins. The reaction of an azide in the presence of an olefin, to give nitrogen and an aziridine, can be induced by heat or light (Figure 3). Loss of nitrogen to give a nitrene could be the first step, or a triazoline intermediate could be initially formed. Triazoline formation is well documented and triazolines are known to decompose to give nitrogen and aziridines[30-32]. The direct addition of nitrenes to olefins is also a well-documented reaction[2,3,33-39]. A decision between the two mechanisms must be made for each reaction studied. From the structure of the product alone, the intervention of a nitrene intermediate can neither be proved nor disproved.

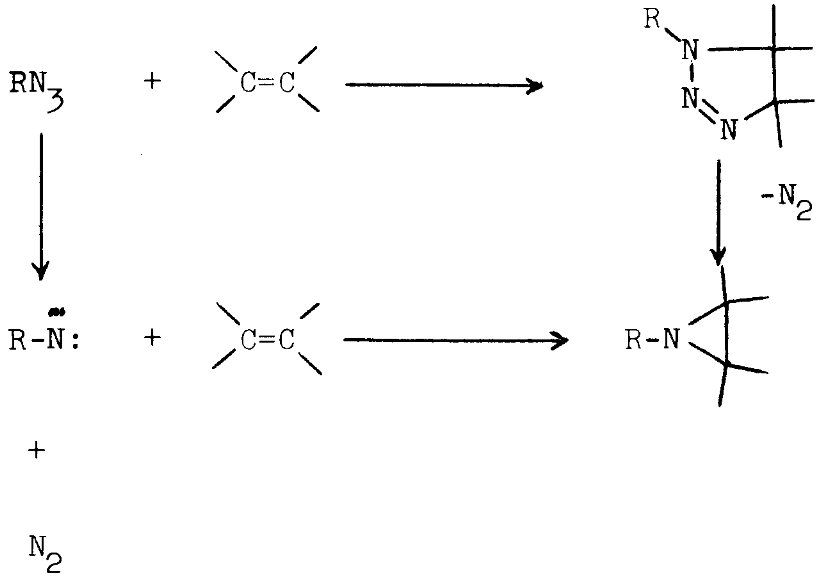
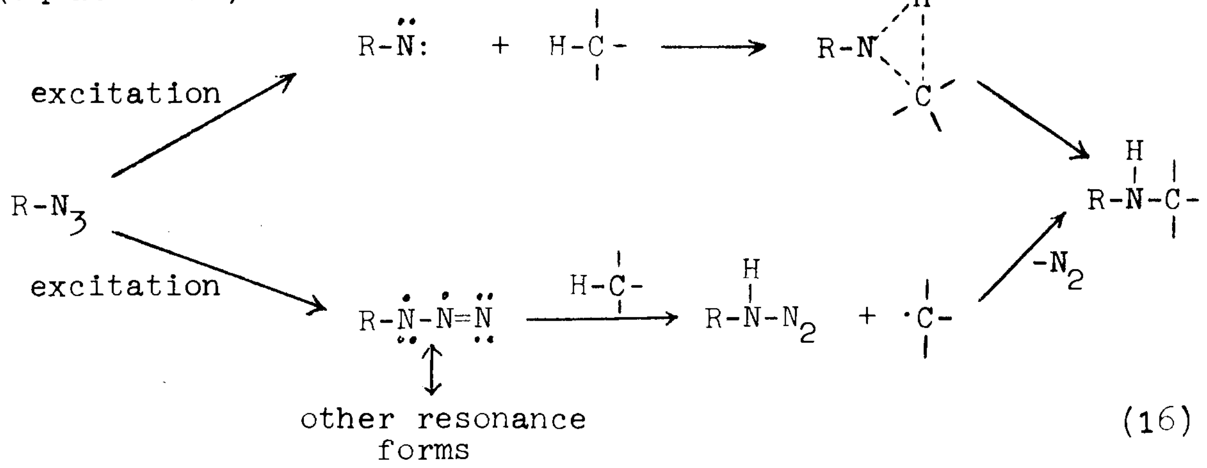


FIGURE 3

A second reaction particularly indicative of a nitrene intermediate is insertion into C-H bonds (equation 16), although even this reaction can be written as an azide reaction (equation 16).



(16)

A number of methods have been used to deduce the intervention of nitrenes in reactions:

1. Kinetic methods

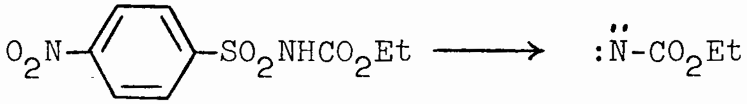
In all known nitrene reactions, the rate-determining step is the formation of the nitrene. In the case of azide or precursors undergoing α-elimination, the rate law is thus first-order in the disappearance of azide or precursor. This is the first kinetic criterion applied to nitrene reactions. For example, the decomposition of benzenesulfonyl azide is first-order in most solvents[40].

2. Spectral verification

As in the carbene field nitrenes have been generated in a frozen matrix at very low temperatures, their ESR and UV spectra observed, and then they have been subsequently allowed to react by raising the temperature[41].

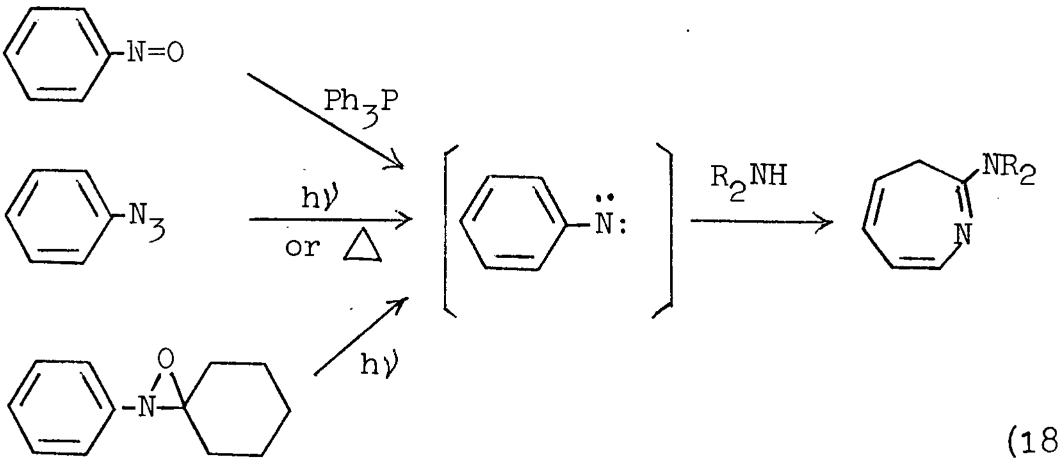
3. Chemical methods

The intervention of a nitrene has been argued to be highly probable in several reactions by generating the species by two or more independent routes, and then demonstrating that the same products or product mixtures resulted in each case. Carboethoxynitrene, for example, can be generated by irradiation[42] or pyrolysis[43,44] of ethyl azidoformate, and by α-elimination of p-nitrobenzenesulfonic acid from N-(p-nitrobenzenesulfonyloxy)-urethan[45] (equation 17). The



(17)

selectivities of the C-H insertion reaction of the species generated in each instance have been compared, and found to be nearly identical[44-48]. Phenyl nitrene seems to be the only likely intermediate in a number of reactions, all leading to 2-dialkylaminodihydroazepines: the pyrolysis[49] or irradiation[50] of phenyl azide, the deoxygenation of nitrosobenzene[51] of nitrobenzene[52], and the irradiation of oxaziranes[53,54] (such as I-34). All of these reactions were carried out in the presence of a dialkylamine (equation 18).



(I-34)

(18)

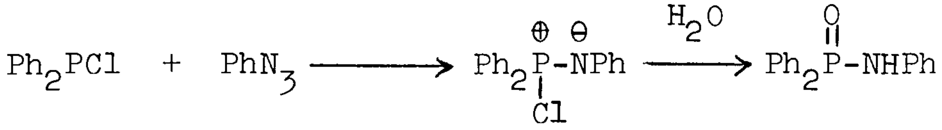
Sometimes, a given precursor gives two distinct sets of products, depending on the mode of decomposition. This can force one to postulate two different mechanisms, only one of which can be the nitrene mechanism. Consideration of the nature of the products, the selectivity with which they are formed, and the mode of decomposition of the precursor might then allow one to assign a nitrene mechanism to one of the reaction paths. Saunders has applied this type of reasoning to the irradiation and thermolysis of triarylmethyl azides[55-57] and Edwards[58] used it to consider the reactions of ethyl azidoformate with dihydropyran.

In the present study we have compared the irradiation of the ylid and the corresponding azide under similar reaction conditions. The involvement of nitrenes in the irradiation of azides is well documented[59].

RESULTS AND DISCUSSION

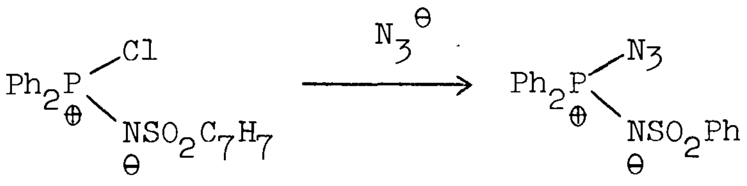
Work with P-chloroiminophosphoranes

Iminophosphoranes with substituents other than aryl on phosphorus are relatively unstable, making the study of their photochemical behavior difficult. Chlorodiphenylphosphine and phenyl azide have been reported to form the expected iminophosphorane which was extremely susceptible to hydrolysis[11] (equation 19).



$$Ph_2PCl \;+\; PhN_3 \longrightarrow Ph_2\underset{Cl}{\overset{\oplus}{P}}\text{-}\overset{\ominus}{N}Ph \xrightarrow{H_2O} Ph_2\overset{O}{\overset{\|}{P}}\text{-}NHPh \qquad (19)$$

The halogen atoms in P-haloiminophosphoranes are also subject to displacement by appropriate nucleophiles (equations 20 and 21).



(20)

$$Cl_3\overset{\ominus}{P}\text{-}\overset{\ominus}{N}SO_2Ph \xrightarrow{NaOCH_3} (CH_3O)_3\overset{\oplus}{P}\text{-}\overset{\ominus}{N}SO_2Ph \qquad (21)$$

Some of the haloiminophosphoranes have been shown to have dimeric rather than monomeric structures, e.g., N-phenyliminotrichlorophosphorane (I-35)[60-62]. There appears to be a consistent correlation between the estimated basicity of a given iminophosphorane and its tendency to dimerize.

Only those iminophosphoranes which carry phosphorus substituents which are electron-withdrawing and nitrogen substituents which are not electron withdrawing appear to be capable of dimerization.

$$Cl_3P{=}N{-}\emptyset$$

(I-35)

The irradiation of N-phenyliminotrichlorophosphorane (I-35) did not give any identifiable products on glpc analysis. Instead a colorless polymeric material(s) (unidentified) deposited on the wall of the cold finger. No azobenzene and/or aniline could be detected.

Thermally, iminotrihalophosphoranes have been reported to undergo reactions similar of other iminotrichlorophosphoranes affording the monomeric form which then undergoes Wittig type reactions with carbonyl compounds[63].

In view of the hydrolytic instability of the P-chloroiminophosphoranes, we centered our attention on the study of their P-triaryl analogs.

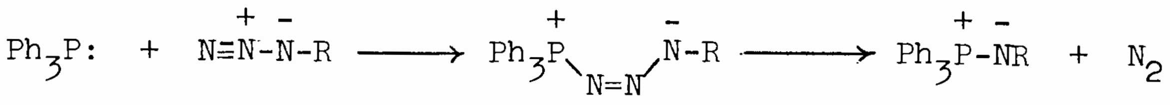
<u>Preparation of Triaryliminophosphoranes</u>

The triaryliminophosphoranes utilized in this study were prepared by warming triarylphosphines with the corresponding azides[64] and recrystallization of the products (equation 22).

$$Ph_3P \quad + \quad RN_3 \longrightarrow Ph_3P{=}NR \quad + \quad N_2\uparrow \qquad (22)$$

This method is applicable to a variety of azides, e.g., benzoyl azide[65], triphenylsilyl azide[66,67], trimethylsilyl azides[68-70], and vinyl azides[71], and the structure of the phosphine component of the reaction can be varied without altering the course of the reaction. For example, tris-(dimethylamino)-phosphine[72], 1,2-bis-(disphenylphosphonio)-ethane[73], trialkylphosphines[74], and trialkylphosphites[75] have been used.

The mechanism of the reaction is known to involve nucleophilic attack by the phosphine on the terminal nitrogen of the azide followed by nitrogen expulsion from the resulting triazine intermediate[76] (equation 23).



$$Ph_3P: + N{\equiv}\overset{+}{N}\text{-}\overset{-}{N}\text{-}R \longrightarrow Ph_3\overset{+}{P}\text{-}N{=}N\text{-}\overset{-}{N}\text{-}R \longrightarrow Ph_3\overset{+}{P}\text{-}\overset{-}{N}R + N_2$$

(23)

Other methods of preparation have been reviewed extensively[1,77,78].

Irradiation of Iminophosphoranes

A) UV spectra of Iminophosphoranes

The UV spectra of all triaryliminophosphoranes studied possess an intense ($\varepsilon = 1.35 \times 10^4 M^{-1}$) broad absorption in the 220-280 nm region due to the aromatic phosphoranes substituents. In addition there is a weak ($\varepsilon = 10^2 M^{-1}$) absorption shoulder centered at 315 nm in photolabile (e.g. I-39) triaryliminophosphoranes. This latter absorption is in the pyrex-transparent region (>300 nm) of the UV spectrum and undoubtedly is receiving irradiation in the present experiments. We attribute this absorption to the n - π^* transition of the ylid nitrogen lone pair. In the photostable ylids the 315 nm absorption is not noticeable.

B) General Irradiation Conditions:

In general, 110 ml of 3×10^{-2}M solutions of ylids in dry solvent were irradiated with a 200 W Hanovia mercury lamp using a pyrex cooling jacket for 3 hours (otherwise specified).

All solvents were distilled over lithium aluminum hydride and the reaction mixtures were made up in a dry box. After transfer to the photocell, the solutions were purged with nitrogen or helium gas dried through 3 trains of anhydrous calcium chloride. The condenser at the purge gas outlet was fitted with an anhydrous calcium chloride drying tube.

C) Photochemically Stable Ylids

Under our reaction conditions, benzenesulfonyl, N-benzoyl, N-carbomethoxy and N-cis-1,2-diphenylvinyl-triphenyliminophosphoranes are photochemically stable. The ylids were recovered quantitatively after irradiation for 8 hours.

This may be attributed to the delocalization of the lone pair of electrons on the nitrogen atom to the resonance-stabilizing sulfonyl, carbonyl or olefinic moiety. This resonance effect also leads to increased stability of these iminophosphoranes to hydrolysis.

The overlapping of vacant phosphorus 3d-orbitals with the filled p-nitrogen orbitals leads to a $d\pi$-$p\pi$ interaction which increases the bond strength as compared to that of a

P-N single bond[96]. Strongly electron-withdrawing groups on the phosphorus increase the bond order of the P-N linkage. In both situations there results a partial positive charge on phosphorus.

D) N-Aryl-triphenyliminophosphoranes

When N-phenyltriphenyliminophosphorane (I-36) was irradiated in dry benzene through a pyrex filter, the reaction mixture changed quickly from pale yellow to orange-red. Two products produced in quantitative yields were triphenylphosphine and azobenzene (equation 24). The quantum yield of the irradiation based on azobenzene formation was 0.7 (see Discussion).

$$\underset{\text{(I-36)}}{2\ Ph_3P{=}NPh} \xrightarrow{h\nu} 2\ Ph_3P + PhN{=}NPh \qquad (24)$$

In several runs of this and other ylid photoreactions the formation of both triphenylphosphine oxide and amine was noted. These products are indicative of the presence of moisture in the photolysis solution.

When phenyl azide was irradiated in benzene, a small yield (5%) of azobenzene was obtained[50]. The major product was aniline. However, it has been reported that when substituted phenyl azides were irradiated in dry benzene high yields of the corresponding azo compounds were produced (Table IV).

TABLE IV

FORMATION OF AZOBENZENE IN THE IRRADIATION OF PHENYL AND SUBSTITUTED PHENYL AZIDES

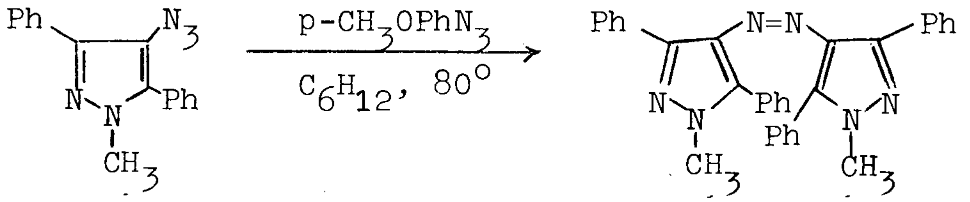
AZIDE	SOLVENT	% YIELD AZOARYL
phenyl	DMSO[79]	0
	ACOH[79]	0
	p-xylene[50]	small
	benzene[79]	5
	diethylamine[50]	0
p-CH_3O-phenyl	benzene[79]	18
	tetrahydrofuran[79]	82
	acetonitrile[79]	82
	DMSO[79]	91
biphenyl	benzene[79]	81
p-chlorophenyl	benzene[79]	0

The formation of azo compounds, the formal dimers of nitrenes, during reactions that are presumed to generate aryl nitrenes, is widely documented, but whether they are in fact formed by dimerization is uncertain.

Although a systematic study has not been made, a comparison of published results for formation of azoaryls upon irradiation of aryl azides reveals that phenyl azides with electron-donating substituents give much higher yields of azo compound than those with electron-withdrawing substituent (Table IV). The fact that the irradiation of p-anisyl azide gave only 18% of azo compound in benzene solution, but 82-91% in solvents, such as tetrahydrofuran, that have unshared electron pairs, suggests that formation of azo compound is favored by factors that stabilize the suspected nitrene intermediate. It is the singlet state of the aryl nitrene that would be thus stabilized[79].

A distinction between direct dimerization of aryl nitrenes and attack of aryl nitrene on aryl azide to form an intermediate tetrazadiene is not possible from available kinetic evidence[59]. Dimerization of highly reactive species formed in low concentrations is improbable; therefore, if dimerization of aryl nitrenes is the source of azo compounds, aryl nitrenes must be of sufficiently low reactivity to survive many collisions with solvent molecules before combining with another aryl nitrene. This view is consistent with the sensitivity of the yield of azo compound to the reactivity of the solvent. Reaction of an aryl nitrene with undecomposed aryl azide is statistically much more probable; although it would also be susceptible to interference by reaction of aryl nitrene with solvent, the reactivity of the aryl nitrene would not need to be so low as in the case of direct dimerization.

The only experimental evidence on the subject lies in the thermolysis of 1-methyl-3,5-diphenyl-4-azidopyrazole[80], which takes place readily at 80°. When thermolyzed alone in cyclohexane, it gives the azopyrazole in 23-36% yield. When it was thermolyzed in the presence of a large excess of p-anisyl azide, which is stable at 80°, it still gave azopyrazole (25% yield) and no detectable mixed azo compound, which would have been expected if the anisyl azide had been attacked by a pyrazolyl nitrene (equation 25).



(25)

25%(plus tar fragmentation products)

No solvent effect on the formation of azo compounds was observed when a number of p-substituted phenyl ylids (Table V) were irradiated in various solvents. In each case high yields of azo derivatives were obtained.

The formation of diaryl azo compounds in these irradiations can be visualized basically in two different mechanisms. The ylids may undergo complete scission of the P=N bond to afford triphenylphosphine, and a reactive aryl nitrene. The latter may couple with another nitrene or react with unreacted ylid to afford an azobenzene derivative (equation 26). Alternatively, the ylid may be photochemically promoted to an electronically excited state. The excited ylid may then react with a ground state ylid and the dimer undergo subsequent fragmentation to products (equation 27).

$$\mathrm{Ph_3P{=}N\text{-}Ph\text{-}R} \xrightarrow{h\nu} \mathrm{Ph_3P} + \mathrm{R\text{-}Ph\text{-}N{:}} \xrightarrow[\substack{\text{or} \\ \mathrm{Ph_3P{=}NPh\text{-}R}}]{\left[\mathrm{R\text{-}Ph\text{-}N{:}}\right]} \mathrm{R\text{-}Ph\text{-}N{=}N\text{-}Ph\text{-}R} \qquad (26)$$

$$\mathrm{Ph_3P{=}N\text{-}Ph\text{-}R} \xrightarrow{h\nu} \left[\mathrm{Ph_3P{=}N\text{-}Ph\text{-}R}\right]^{*} \xrightarrow[\mathrm{Ph_3P{=}NPh\text{-}R}]{} 2\ \mathrm{Ph_3P} + \mathrm{R\text{-}PhN{=}NPh\text{-}R} \qquad (27)$$

A number of alkenes were used as solvents hoping to trap the aryl nitrenes (Table V). When cumene was used in cyclohexene in an attempt to trap any radical formed in the irradiation, only a trace amount (1%) of dicumyl was detected. It is likely that this results from P-N cleavage[25].

Phenyl nitrene[49,50,82-84] is reported to undergo ring expansion in the presence of bases, such as diethylamine, to afford azepine derivatives. Irradiations of both phenyl azide and N-phenyltriphenyliminophosphorane (I-36) in diethylamine were thus carried out separately, under identical reaction conditions. With phenyl azide, 2-diethylamino-3H-azepine was indeed isolated. No azepine was detected from irradiation of the ylid.

Although intermolecular addition and insertion reactions are inefficient processes for phenyl-nitrene[50,85,86] intramolecular insertions have been reported. It was thus hoped that intramolecular abstraction or insertion would be a

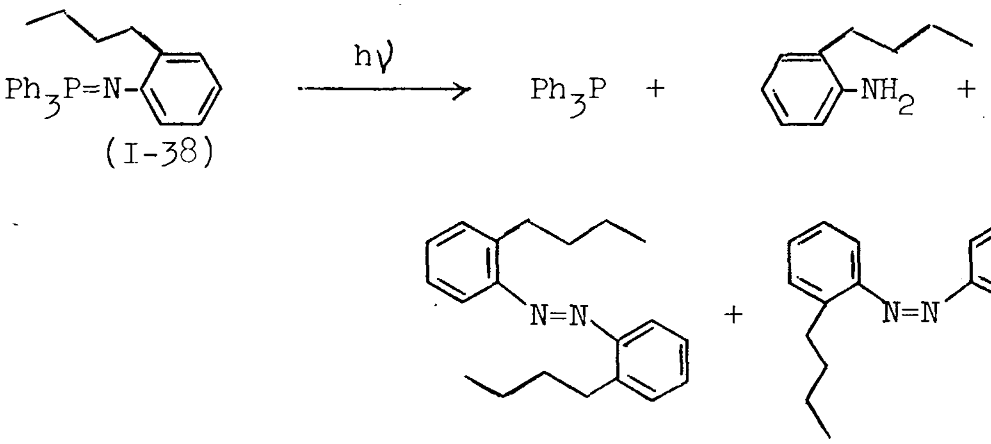
TABLE V

IRRADIATION OF N-PHENYLTRIPHENYLIMINOPHOSPHORANE (I-36)

SOLVENT	RX. TIME	PRODUCTS
BENZENE	1 h	Ph_3P + PhN=NPh (100%) (100%)
CYCLOHEXENE	3 h	Ph_3P + aniline + PhN=NPh (78%) (17%) (55%)
STYRENE IN CYCLOHEXENE	5 h	Ph_3P + Ph_3P=O + aniline + PhN=NPh (79%) (8%) (7%) (73%)
DIHYDROPYRAN	3 h	Ph_3P + Ph_3P=O + aniline + PhN=NPh (64%) (13%) (12%) (34%)
1,1,2,2-TETRAMETHYL-ETHYLENE	4 ½ h	Ph_3P + PhN=NPh (93%) (70%)
ACETONITRILE	6 h	Ph_3P + PhN=NPh (80%) (75%)
CUMENE IN CYCLOHEXENE	4 h	Ph_3P + PhN=NPh + dicumyl (87%) (83%) (1%)
DIETHYLAMINE	12 h	Ph_3P + PhN=NPh + no azepine (80%) (78%)

suitable reaction for the detection of aryl nitrene. Three N-ortho-substituted phenyltriphenyliminophosphoranes were prepared and irradiated under identical reaction conditions (Table VI).

In no case was there any C-H insertion of the suspected aryl nitrene into the aliphatic appendages of I-37 or I-38 or the aryl C-H of I-39. Whereas the irradiation of I-37 and I-39 each gave only one azo compound, two azobenzene derivatives (equation 28) with the same molecular weight (M.W. 294) but different glpc retention times were detected



(I-38)

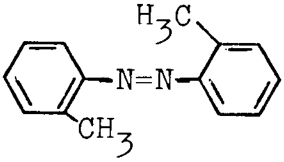
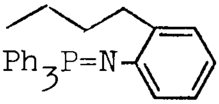
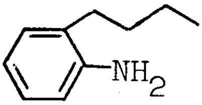
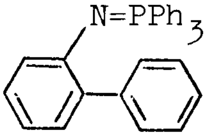
(28)

in the photoreaction of I-38. The ratio of these two derivatives fluctuated during the reaction time. The one with shorter retention time decreased while the other increased after the irradiation was stopped. Although there is little doubt they are *cis*- and *trans*-isomers, they failed to crystallize.

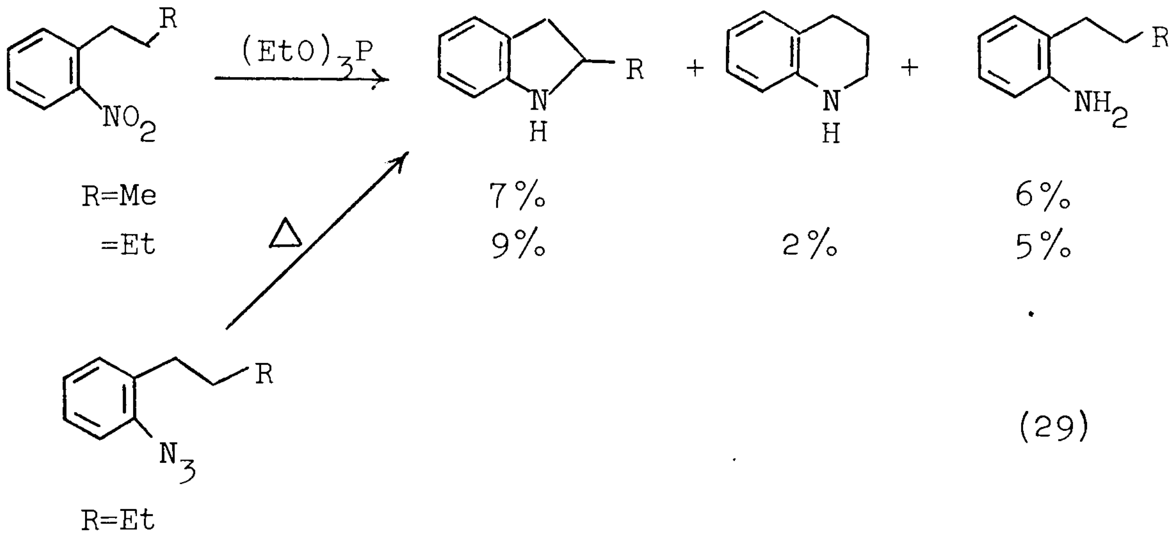
These results contrast with the products observed upon the reduction of o-propyl-, o-butyl, o-cyclohexyl-[87], and

TABLE VI

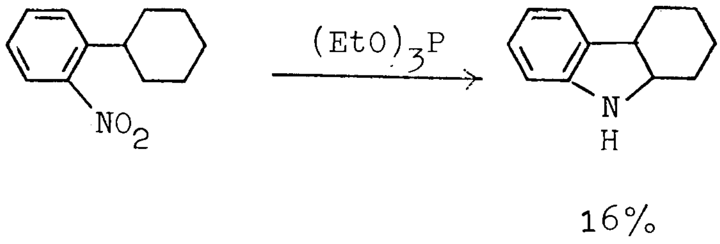
IRRADIATION OF ORTHO-SUBSTITUTED N-PHENYLTRIPHENYLIMINOPHOSPHORANES IN BENZENE

YLID	TIME	PRODUCTS
o-CH_3-Ph-N=PPh_3 (I-37)	3h	Ph_3P, (81%)  (75%)
 (I-38)	3h	Ph_3P, (85%)  , (5%) azobenzene derivatives (70%)
 (I-39)	6h	Ph_3P, Ph_3PO, o-NH_2-Ph-Ph (69%)(7%) (2%) azobiphenyl (93%)

o-ethyl nitrobenzene[88] with triethylphosphite which give minor but detectable amounts of C-H abstraction and insertion products attributable to the intermediate nitrenes (equations 29 and 30).



(29)



(30)

The intermediacy of nitrenes in these deoxygenations were confirmed by Smolinsky and Feuer[89] who compared the product distribution of such deoxygenations with that of the corresponding azides.

Considering the low yields of the nitrene insertion products in the azide irradiations, it is likely that the competing reaction of the ylid with the nitrene (if formed) to afford azo compounds may result in yields of nitrene insertion products too low to be detected by glpc.

Formation of carbazole from the irradiation of 2-azidobiphenyl is an efficient reaction[90], especially when the reaction is under singlet sensitization[91]. The involvement of nitrene in this irradiation has recently been further confirmed by flash irradiation[92] and isolation of azepine with nucleophilic trapping agent[93]. These observations prompted the preparation and irradiation of N-2-biphenyltriphenyliminophosphorane (I-39).

Irradiation of (I-39) in benzene, in dioxane, and in ether afforded azobiphenyl (I-40) in near quantitative yields. However, the other product, triphenylphosphine, underwent a secondary photodecomposition (20%)[19]. This was confirmed by separate irradiation of triphenylphosphine. There seemed to be no solvent effect on the course of the irradiation (Table VII), and carbazole was not detected. This could be indicative of the absence of a nitrene intermediate[79], which was reported to give different product distributions in different solvents. A number of sensitizers and quenchers were also used but failed to affect any change in the product distributions (Table VII).

When dried air was used as purge gas and the irradiation conducted in benzene, carbazole was formed in 26.4% yield (Table VIII). In the presence of oxygen, it was presumed that two reactions occurred. In addition to the usual photodecomposition to afford azobiphenyl (I-40) and triphenyl-

TABLE VII

SOLVENT EFFECT ON PRODUCT DISTRIBUTION OF THE IRRADIATION OF YLID I-39 (% YIELD)

COMPOUNDS	BENZENE	ANTHRACENE IN BENZENE	DIOXANE	ETHER	PIPERYLENE IIN ETHER
biphenyl	ND	ND	4.0 ± 0.5 %	ND	ND
o-aminobiphenyl	2.0 ± 0.5 %	1.0 ± 0.5 %	ND	2.0 ± 0.5 %	1.0 ± 0.5 %
carbazole	ND	ND	ND	ND	ND
Ph_3P	69 ± 5 %	71 ± 5 %	78 ± 5.0 %	80 ± 5 %	85 ± 5 %
Ph_3PO	7.3 ± 0.5 %	5.0 ± 0.5 %	1.2 ± 0.5 %	10.0 ± 0.5 %	5.0 ± 0.5 %
azobiphenyl	93 ± 5.0 %	90 ± 5.0 %	100 ± 5.0 %	90 ± 5.0 %	95 ± 5.0 %

ND (Not Detected) < 0.1%

TABLE VIII

EFFECT OF PURGE GAS ON PRODUCT DISTRIBUTION OF IRRADIATION OF I-39 IN BENZENE (% YIELD)

COMPOUNDS	HELIUM	AIR	OXYGEN
o-amino-biphenyl	2.0 ± 0.5 %	3.7 ± 0.5 %	7.3 ± 0.5 %
biphenyl	ND	ND	ND
o-nitrosobiphenyl	ND	trace	5.0 ± 0.5 %
carbazole	ND	26.4 ± 0.5 %	19.2 ± 0.5 %
PhP	69 ± 5 %	8.3 ± 0.5 %	ND
Ph_3PO	7.3 ± 0.5 %	76 ± 5 %	91 ± 5 %
azobiphenyl	93 ± 5 %	41 ± 5 %	20 ± 5 %

ND (Not Detected) < 0.1%

phosphine, ylid I-39 probably underwent photooxidation to give triphenylphosphine oxide and o-nitrosobiphenyl (I-40). The latter was then deoxygenated by triphenylphosphine to afford triphenylphosphine oxide, o-aminobiphenyl (I-42) and carbazole (I-43)[95,96] (Figure 4).

This speculation was reinforced by the observation that the yield of azobiphenyl decreased when pure oxygen was used as purge gas (Table VIII).

Since it has been reported[97-99] that 2-aminobiphenyl (I-42) undergoes oxidative cyclization to form carbazole we wished to determine if 2-aminobiphenyl was a precursor of carbazole in our photo-reaction. Accordingly a solution of 2-aminobiphenyl was irradiated in an equimolar amount of triphenylphosphine with oxygen as purge gas. No carbazole was detected (glpc) and the amine was unreacted.

It should be pointed out that azobiphenyl could also be formed by the reaction of 2-nitrosobiphenyl[96] with ylid I-39. Nitrobenzene and nitrosobenzene were observed products of irradiation of N-phenyltriphenyliminophosphorane (I-36) in the presence of air. When irradiation of N-phenyltriphenyliminophosphorane (I-36) was repeated with oxygen as purge gas, carbazole was formed in 15±5 % yield (Table IX). Small amounts of nitrosobenzene and nitrobenzene were also detected.

The ylid remained unreacted in refluxing benzene under an oxygen atmosphere. No aniline, nitrosobenzene, nitrobenzene or triphenylphosphine oxide was detected by glpc.

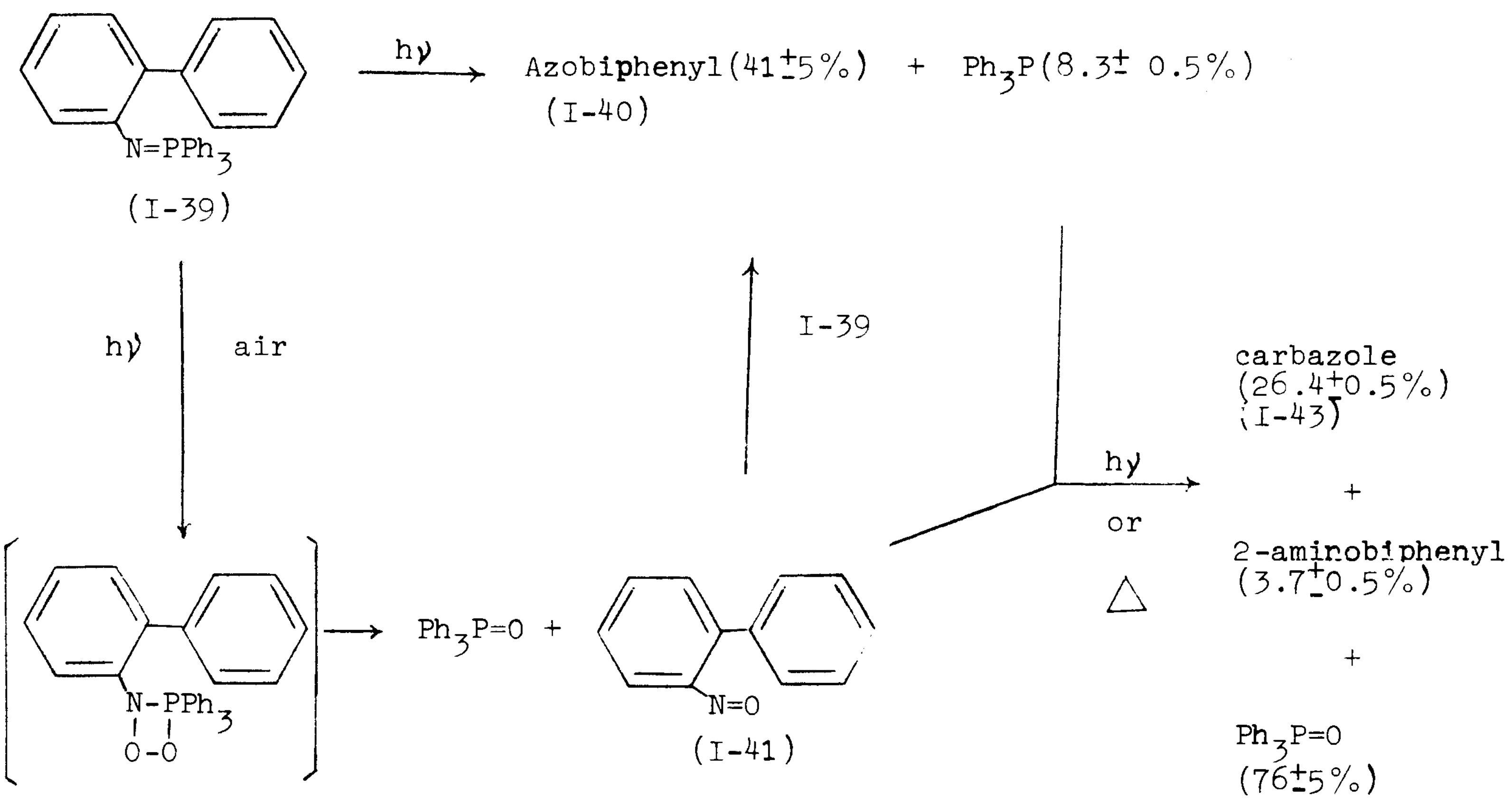

N=PPh3
(I-39)
hν
Azobiphenyl(41±5%)
(I-40)
+
Ph3P(8.3± 0.5%)
hν
air
I-39
N-PPh3
O-O
Ph3P=O +
N=O
(I-41)
hν
or
△
carbazole
(26.4±0.5%)
(I-43)
+
2-aminobiphenyl
(3.7±0.5%)
+
Ph3P=O
(76±5%)

FIGURE 4

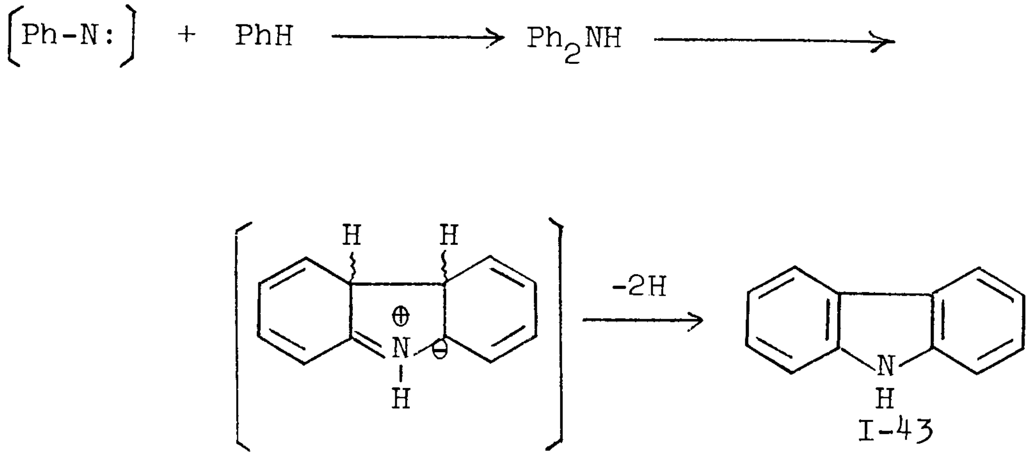
TABLE IX

EFFECT OF OXYGEN ON PRODUCT DISTRIBUTION OF THE IRRADIATION OF YLID I-36 (% YIELD)

COMPOUNDS	HELIUM	OXYGEN
carbazole	ND	15 ± 5 %
aniline	ND	5 ± 2 %
azobenzene	94 ± 5 %	5 ± 2 %
Ph_3P	90 ± 5 %	ND
Ph_3PO	ND	90 ± 5 %
nitrobenzene	ND	trace
nitrosobenzene	ND	15 ± 5 %

ND (Not Detected) $<$ 1%

Formation of carbazole has been reported in the gas-phase thermolysis of phenyl azide[98], which has been postulated to involve a novel addition of phenyl nitrene to benzene (equation 31)



(31)

It has been reported[99] and confirmed under our reaction conditions that diphenylamine underwent photolytic cyclization to carbazole.

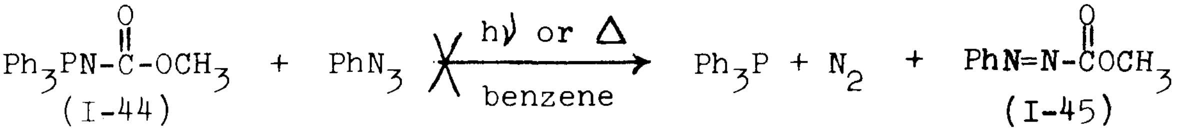
These results seemed to indicate that aryl nitrenes are involved when the irradiation was performed in the presence of oxygen, with aryl nitro or aryl nitroso compounds as the precursors.

In order to seek evidence as to the intermediacy of a nitrene or an excited ylid (presumably a diradical) in the irradiation of triphenyliminophosphoranes, the following experiments were attempted.

a. Trapping of Aryl nitrene by a Photostable Ylid

To determine whether aryl nitrenes could be trapped by ylid, phenyl nitrene was generated photochemically and thermally from phenyl azide in the presence of a photochemically stable ylid (I-44).

The ylid remained unreacted under both sets of conditions and no carbomethoxy azobenzene (I-45) was formed (equation 32).

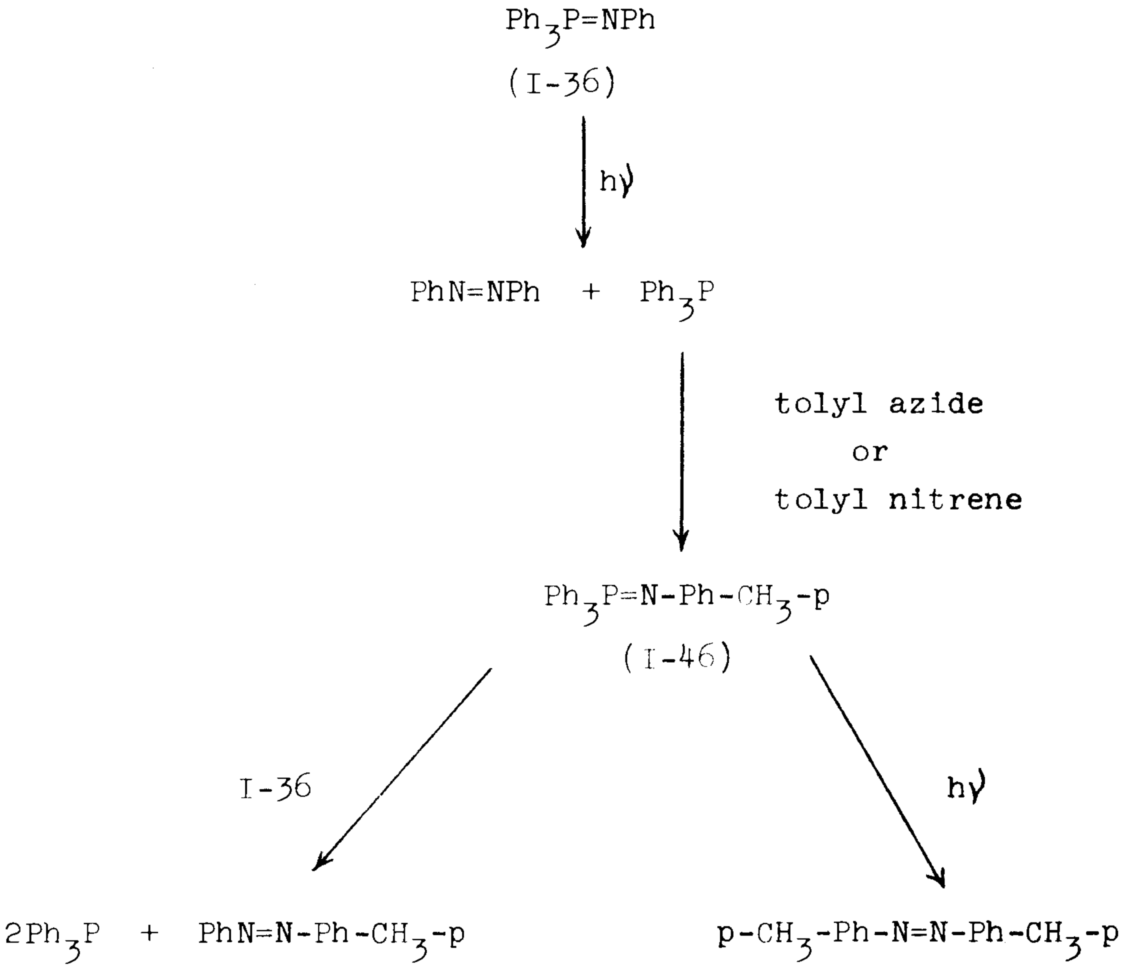


$$\underset{(\text{I-44})}{Ph_3PN-\overset{O}{\overset{\|}{C}}-OCH_3} + PhN_3 \cancel{\xrightarrow[\text{benzene}]{h\nu \text{ or } \Delta}} Ph_3P + N_2 + \underset{(\text{I-45})}{PhN{=}N-\overset{O}{\overset{\|}{C}}OCH_3} \qquad (32)$$

b. Trapping of Aryl nitrene by a Photolabile Ylid

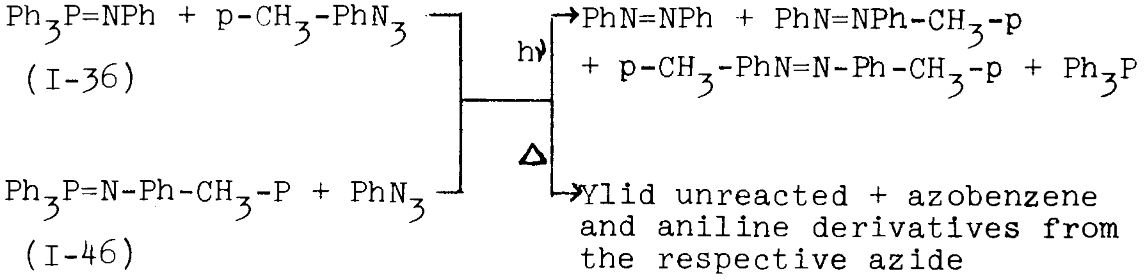
When an aryl nitrene (from tolyl azide) was generated thermally in the presence of the photochemically reactive ylid I-36, the ylid remained unreacted. However, in the attempt to generate the same aryl nitrene photochemically in the presence of the photolabile ylid I-36, three azobenzene derivatives were formed. The same result was observed with N-tolyltriphenyliminophosphorane (I-46) and phenyl azide (equation 33).

The formation of the asymmetric azobenzene was apparently due to the photodimerization of ylid I-32 and ylid I-46 (Figure 5). The latter was formed between the unreacted azide and triphenylphosphine generated by the ylid irradiation.



$Ph_3P{=}NPh$
(I-36)
hν
$PhN{=}NPh$ + Ph_3P
tolyl azide
or
tolyl nitrene
$Ph_3P{=}N\text{-}Ph\text{-}CH_3\text{-}p$
(I-46)
I-36
hν
$2Ph_3P$ + $PhN{=}N\text{-}Ph\text{-}CH_3\text{-}p$
$p\text{-}CH_3\text{-}Ph\text{-}N{=}N\text{-}Ph\text{-}CH_3\text{-}p$

FIGURE 5



(33)

To confirm this, a 1:1 mixture of ylid I-36 and ylid I-46 were irradiated under similar reaction conditions. The same three azobenzenes were formed in the ratio of 1:2:1. The same result was obtained with ylids I-36 and I-37 (equation 34).

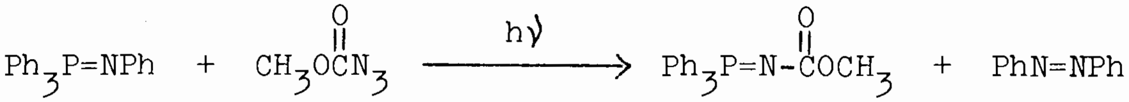
$$\underset{(\text{I-36})}{Ph_3P{=}NPh} + \underset{(\text{I-46 or I-37})}{(\text{p- or o-})CH_3\text{-}Ph\text{-}N{=}PPh_3}$$

$$\xrightarrow{h\nu} \underset{1}{PhN{=}NPh} \; + \; \underset{2}{PhN{=}NPhCH_3} \; + \; \underset{1}{CH_3PhN{=}NPhCH_3}$$

1 : 2 : 1

(34)

To further substantiate the formation of ylid I-46 as an intermediate (Figure 5), we repeated the experiment with ylid I-36 and an azide which would produce a photochemically stable ylid with triphenylphosphine and thus could be isolated. Indeed, when methyl azidoformate was irradiated with ylid I-36, ylid I-44 was formed along with azobenzene (equation 35). Again ylid I-36 remained unreacted when the reaction was repeated thermally.



$$\underset{(\text{I-32})}{Ph_3P{=}NPh} + CH_3O\overset{\overset{O}{\|}}{C}N_3 \xrightarrow{h\nu} \underset{(\text{I-44})}{Ph_3P{=}N{-}\overset{\overset{O}{\|}}{C}OCH_3} + PhN{=}NPh \qquad (35)$$

These results and the previous findings that irradiation of N-aryltriphenyliminophosphoranes does not afford aryl amine, and that N-2-biphenyltriphenyliminophosphorane (I-39) does not undergo photochemical sensitization to yield carbazole as does the corresponding azide, indicate that nitrene is not involved as the reactive intermediate in the irradiation of N-aryl ylids.

Thus it seems likely that irradiation of N-aryltriphenyliminophosphoranes affords photoexcited ylids which combine with a ground state ylid and then fragment (equation 36).

$$Ph_3P{=}N{-}Ar \xrightarrow{h\nu} \left[Ph_3P{=}N{-}Ar\right]^* \xrightarrow{Ph_3P{=}NAr} 2\ Ph_3P + ArN{=}NAr \qquad (36)$$

E. N-Alkyltriphenyliminophosphoranes

These ylids hydrolyze readily with the moisture in the atmosphere (equation 37). As one might expect resonance stabilizing and sterically hindered substituents on the alkyl carbon increase the resistance to hydrolysis. Thus, while N-β-phenethyltriphenyliminophosphorane (I-47) and N-cyclohexyltriphenyliminophosphorane (I-54) are readily hydrolyzed, and N-benzyltriphenyliminophosphorane (I-48) is slowly hydrolyzed, N-trityltriphenyliminophosphorane (I-49) is stable to moisture in the atmosphere.

$$Ph_3P{=}N{-}R \xrightarrow{H_2O} Ph_3PO + RNH_2 \qquad (37)$$

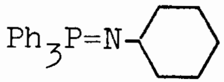
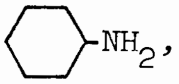
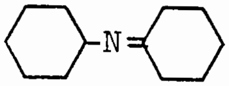
R = alkyl

The products obtained by irradiation of the N-alkyl ylids (Table X) were different than expected from a nitrene intermediate. The irradiation of ylid I-47 gave ethylbenzene. Alkanes are not usually formed from alkyl nitrenes produced via azide decomposition.

When ylid I-48 was irradiated in benzene or ether, the major products detected by glpc were triphenylphosphine, N-benzyl-benzaldimine (I-50), benzylamine (I-51) and triphenylphosphine oxide. The imine I-50 isolated was apparently the condensation product of amine I-51 and benzaldehyde formed by hydrolysis of benzaldimine (I-52). The latter was presumably formed by abstraction of the benzylic proton (Figure 6).

TABLE X

PRODUCTS OF IRRADIATION OF N-ALKYLTRIPHENYLIMINOPHOSPHORANES

YLIDS	SOLVENTS	TIME	PRODUCTS			
$Ph_3P{=}NCH_2Ph$ (I-48)	benzene	12 h	Ph_3P, Ph_3PO, (80%)(10%)	$PhCH_2N{=}CHPh$, (48%)	$PhCH_2NH_2$ (3%)	
$Ph_3P{=}NCPh_3$ (I-49)	benzene	6 h	Ph_3P $Ph_2C{=}NPh$ (80%) (65%)			
 (I-54)	ether	6 h	Ph_3P, Ph_3PO, (70%)(12%)	 (5%)	 (60%)	

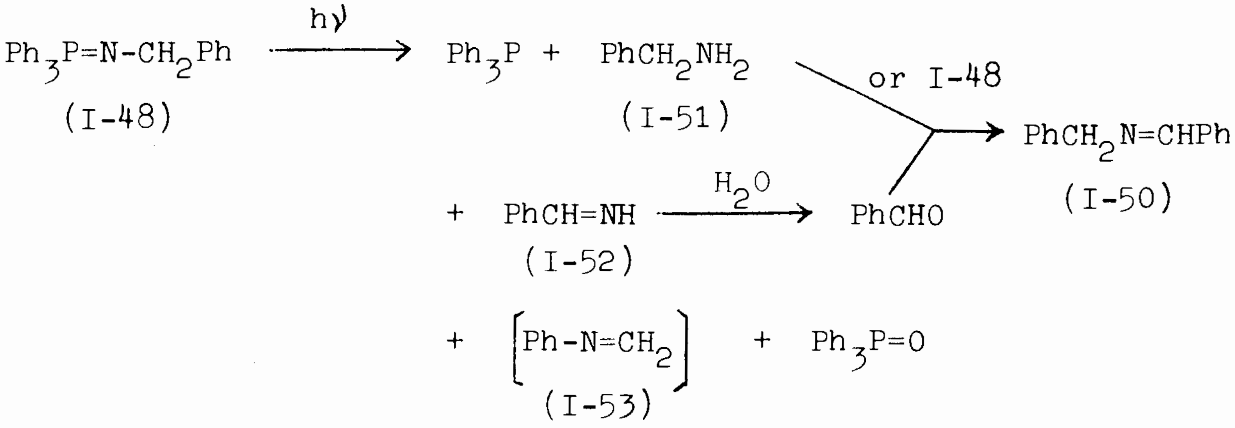


FIGURE 6

Imine I-53 is formed by phenyl migration as in the azide irradiation[100]. Imine I-53 is unstable and an attempt to synthesize it by condensation of aniline with formaldehyde gave only the trimer. This trimer was not found in the reaction mixture of the irradiation of ylid I-48, but imine I-53 may well have polymerized.

The migratory aptitude of the phenyl and the hydrogen in the irradiation of benzyl azide is 1:1[100]. This could explain the low yield (45%) of imine I-50.

In the irradiation of N-cyclohexyltriphenyliminophosphorane (I-54), only hydrogen migration is expected. Accordingly, ylid I-54 gave triphenylphosphine, N-cyclohexylcyclohexanone imine (I-55), cyclohexylamine (I-56) and triphenylphosphine oxide as major products (Figure 7). Substracting the amount of cyclohexylamine (I-56) formed from the hydrolysis of the ylid (equimolar to triphenylphosphine oxide formed) revealed that the product distribution of cyclohexanone imine (I-57) and amine I-56 formed from the photoreaction is in good agreement with that of the corresponding azide[100,101].

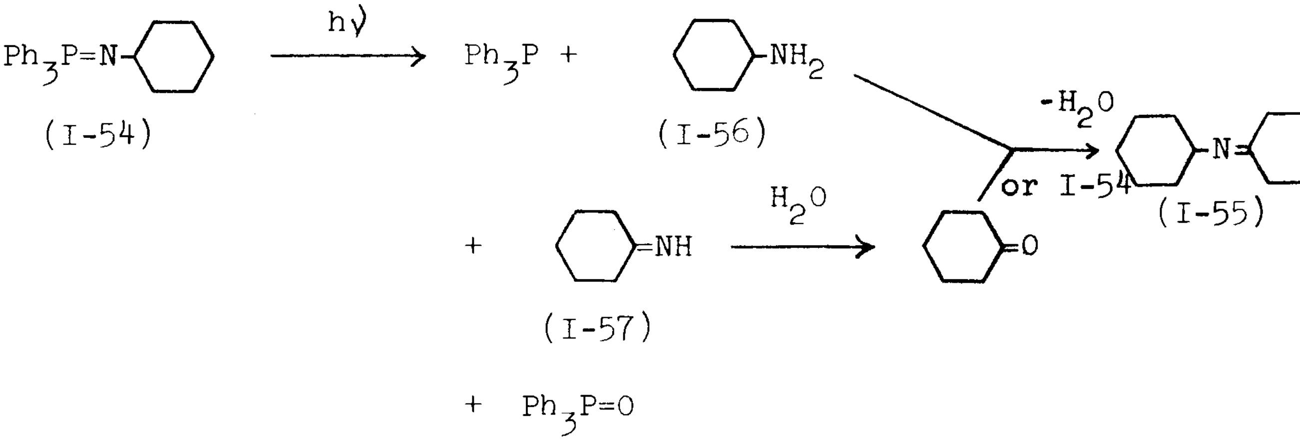


FIGURE 7

Irradiation of N-trityltriphenyliminophosphorane (I-49), yielded only triphenylphosphine and N-phenylbenzophenone imine (I-58) (equation 38). The latter is the only product in the irradiation and thermolysis of trityl azide[55-57], where tritylnitrene was postulated as the reactive intermediate.

$$\underset{\text{(I-49)}}{Ph_3P{=}N{-}CPh_3} \xrightarrow{h\nu} Ph_3P + \underset{\text{(I-58)}}{PhN{=}CPh_2} \qquad (38)$$

F. Wavelength Dependence of the Irradiation of Triphenyliminophosphoranes

When the photostable (with pyrex, > 300 nm) ylid I-44 was irradiated in ether for 8 hours in a quartz (> 200 nm) cell, benzene was formed in good yield (see experimental) and no triphenylphosphine or other products could be detected.

With ylid I-36 under similar conditions the yield of triphenylphosphine and azobenzene decreased significantly to 40% and 41% respectively (from 100% and 100% respectively in pyrex (Table V)) with the formation of benzene. The photochemical behavior of triphenyliminophosphoranes is governed by the substituent on the nitrogen moiety. While the N-sulfonyl, N-carbonyl, or N-vinyl substituent completely stablize iminophosphoranes against photolysis, N-aryl substitution does not.

The wavelength dependence of the photoreactions of these ylids may be explained on the basis of two different types of electronic excitation from different molecular orbitals. Nagao[17] and Durr[20] have assigned P=C cleavage to n-π^* excitation of the non-bonding electrons on the anionic carbon ($\overset{+}{P}$-$\overset{-}{C}$) and phosphorus-phenyl cleavage to π-π^* excitation of a phenyl group. Excitations of an electron from the high-energy non-bonding orbitals (n) to the lowest unoccupied MO (π^*) requires less energy than any other electronic transition. This n-π^* transition is responsible for the long wavelength, low intensity ultraviolet absorption of ketones.

From the energy of the light source applied, the λ_{max} of P=N (315 nm), and the correlation of substituent effects with basicity, as well as susceptibility to hydrolysis and irradiation of iminophosphoranes, it seems reasonable to make similar assignments in the irradiation of triphenyliminophosphoranes.

The results we have accumulated for N-aryltriphenyliminophosphoranes photoreactions allow formulation of a possible mechanistic scheme for the irradiation.

Since ylid I-36 (or I-46) did not react with tolyl (or phenyl) nitrene and since no trapping experiment for aryl nitrenes from the irradiation of these N-aryl ylids was successful, aryl nitrenes are apparently not the reactive intermediates. If phenyl nitrene were present (Figure 8), triphenylphosphine should exhibit a quenching effect on the irradiation but not affect the excited ylid mechanism.

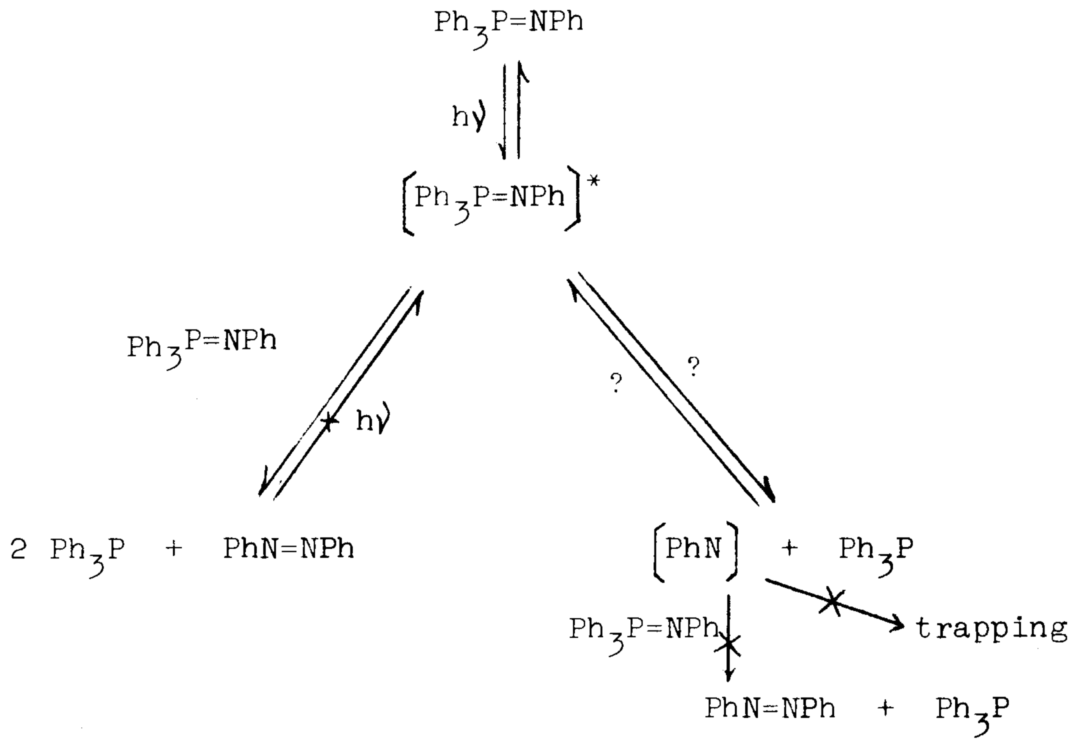
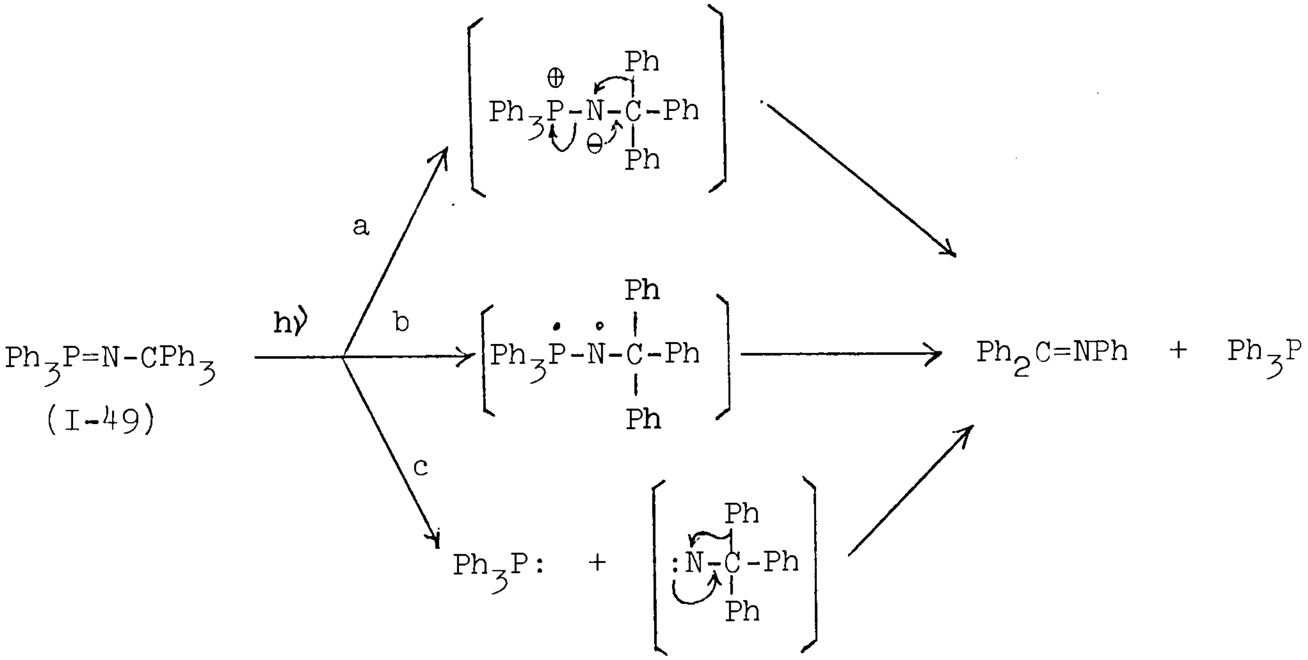


FIGURE 8

From the results of the irradiation of N-alkyltriphenyliminophosphoranes, it seems possible that alkyl nitrenes may indeed be involved. Ylids derived from trityl azides should be the best candidates for further mechanistic studies. First of all, ylids like I-49 (and its derivatives) are least susceptible to hydrolysis. Secondly, the same product, namely benzophenone anil, was obtained as from the azide analog. The fact that the anticipated azo and/or azo-decomposition products were not detected[22] in the irradiation of ylid I-49 is very encouraging (equation 39). Thirdly, the mechanism of azide photolysis has been extensively studied.



(39)

With trityl azide, the substituents on the phenyl rings have practically no effect on the migratory aptitudes in the photolysis reaction[56] in contrast to the thermal rearrangement where electron-donating substituents on the phenyl ring have been shown to favor phenyl migration and electron-withdrawing groups to hinder it[55]. It was concluded on this basis that the thermal rearrangement was a concerted process, but that the photochemical reaction proceeded through a discrete nitrene intermediate. (Table XI)

TABLE XI[55]

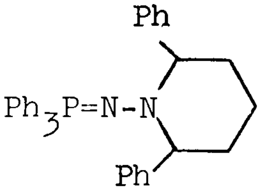
MIGRATORY APTITUDES FOR PYROLYSIS OF TRITYL AZIDES

X	Migratory aptitudes $p\text{-}x\text{-}C_6H_4$ vs C_6H_5	% Yield imines
$(CH_3)_2N$	6.7	70
CH_3O	2.5	70
CH_3	1.8	66
H	1.0	75
Cl	0.39	43
NO_2	0.20	75

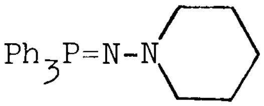
Numerous attempts have been made to identify the products of irradiation of triphenylphosphinazenes of structure I-58. Irradiation of this type of ylid,

$Ph_3P=N-NR_2$

I-58



I-59



I-60

e.g. I-59 and I-60, ylids triphenylphosphine, but no other identifiable products were detected (such as the degradation products from the tetrazene, $R_2N-N=N-NR_2$). Attempts should be made with derivatives which could afford identifiable products in order to differentiate the excited ylid mechanism from the generation of N-amino nitrenes.

EXPERIMENTAL

General Description of Equipments and Services

Infrared spectra were recorded with Unicam SP200 or Beckman IR-12 spectrophotometer. The nmr spectra were taken on a Varian A-56-60 spectrometer with tetramethylsilane as an interval standard. Ultraviolet spectra were recorded on either Unicam SP/800 or Cary 14 spectrophotometer.

Mass spectra were obtained on a Perkin-Elmer Hatachi spectrometer using an ionization voltage of 70eV and an inlet temperature of 175-200°.

General Description of Irradiation

All solvents were distilled over lithium aluminum hydride and the reaction mixtures were made up in a dry-box. After transferred to the photocell, the reaction mixtures were purged with dry helium for 1 hour before being irradiated.

The photolysates were purged with helium gas (unless otherwise specified) which was dried by passing through 3 trains of anhydrous calcium chloride. A condenser was fitted on the purge gas outlet with an anhydrous calcium chloride drying tube.

A 200 W Hanovia mercury lamp with the appropriate filter cooling jacket was used as the source of irradiation.

Analyses were carried out by gas-liquid partition chromatography on a Varian Areograph Autoprep and Series 1200 gas chromatography units. The column used was 6 ft. X 1/4 in., 20% SE-30 silicon oil stationary phase on 100-200 mesh HMDS washed chromosorb W support. Each analysis was temperature programmed from 60°-$300^{\circ}C$ at a rate of $4^{\circ}C$ per minute.

New compounds were either analyzed by GC-mass spectrometer or isolated by preparative GC for further analysis.

Elemental analyses were performed on a Perkin-Elmer 240 micro-analyzer in the Simon Fraser University laboratory.

Yield determination was calculated by means of an octadecane internal standard (I.S.) with the following equation:

$$\text{Specific Response} \doteq \frac{\text{Wt. X}}{\text{Response X}} : \frac{\text{Wt. I.S.}}{\text{Response I.S.}}$$

i.e.

$$\text{Wt. X} = \text{Specific Response X } \frac{\text{Response X}}{\text{Response I.S.}} \text{ X Wt. I.S.}$$

Preparation of N-phenyltrichloroiminophosphorane[60]

Equimolar quantities of aniline and phosphorus pentachloride were refluxed in carbon tetrachloride at 70-75°C for 2 hours. After removal of solvent under vacuum, the residue was dissolved in dry benzene for irradiation without further purification.

Irradiation of N-phenyltrichloroiminophosphorane

A 110 ml benzene solution of (~ 10 mM) N-phenyltrichloroiminophosphorane was irradiated with a pyrex filter for 12 hours. Glpc analysis indicated no formation of azobenzene and/or aniline. However, some colorless polymeric material(s) (unidentified) deposited on the wall of the cold finger.

Preparation of Azides[105,6]

All azides were prepared by conventional methods reported in the literature cited (see text). Purification was accomplished by passing a petroleum ether solution of the crude azide through a silica gel column instead of distillation (for liquid azides) or recrystallization(for solid azides).

Identification of azido group was indicated by the IR band at 2100 cm^{-1} and the complete identification was performed on the corresponding ylid formed.

Preparation of N-substituted Triphenyliminophosphoranes

Staudinger's method[64] was adopted for the preparation of the following ylids by reacting triphenylphosphine with the corresponding azides (Table XII).

A benzene solution of various azides was added dropwise under dry conditions to a benzene solution of triphenylphosphine in 1.1:1 molar ratio, respectively. The mixture was left stirring overnight (or until nitrogen evolution ceased). After evaporation of solution, the ylid was crystallized twice from benzene-petroleum ether.

TABLE XII

LIST OF IMINOTRIPHENYLPHOSPHORANES PREPARED

Ylid	m.p.	m.p.(lit.)
N-benzenesulfonyl	156-7°C	157-8°C[103]
N-benzoyl	196-7°C	196-7°C[103]
N-carboethoxy (I-47)	135-6°C	136-7°C[103]
N-carbomethoxy (I-44)	136-7°C	136-7°C[103]
N-*cis*-1,2-diphenylvinyl	157-9°C (decomp.)	157-7.5°C[103]
N-phenyl (I-36)	133-4°C	131-2°C[103]
N-o-tolyl (I-37)	130-1°C	129-30°C[103]
N-p-tolyl (I-46)	135-6°C	135-6°C[103]
N-o-n-butyl (I-38)	134-5°C	Calc. for $C_{28}H_{28}NP$ 409(M^+);
N-2-biphenyl (I-39)	140-1°C	Calc. for $C_{30}H_{24}NP$ 429(M^+); Found 429(M^+)
N-β-phenethyl (I-47)	105-8°C	Calc. for $C_{26}H_{24}NP$ 381(M^+); Found 381(M^+)
N-benzyl(I-48)	112-3°C	Calc. for $C_{25}H_{22}NP$ 367(M^+); Found 367(M^+)
N-trityl (I-49)	228-9°C	228-9°C[104]
N-cyclohexyl (I-54)	71-3°C	Calc. for $C_{24}H_{26}NP$ 359(M^+); Found 359(M^+)

Irradiation of Photochemically Stable Ylids

A 30 mM solution of the ylid in 110 ml of benzene (with octadecane as internal standard) was irradiated for 8 hours through a pyrex filter cooling jacket. The reaction was concentrated to 10 ml and subjected to glpc analysis. The ratio of ylid to octadecane remained unchanged from the initial concentrations and no triphenylphosphine was detected. Evaporation of the solvent and recrystallisation from benzene/petroleum ether gave 90% recovery of the ylid.

Irradiation of Ylid I-36 in Various Solvents

A 25-30 mM solution (clear to pale yellow) of each ylid in benzene (110 ml) with octadecane as internal standard was irradiated for 1 hour through a pyrex filter cooling jacket. The photolysate (brick red to brown) was concentrated to 10 ml and subjected to glpc analysis. The identity of azoaryl, aryl amine, triphenylphosphine and triphenylphosphine oxide was determined by mixed injection with authentic samples. The yields given in Table V were determined as described above. The photoreactions of I-36 in diethylamine was carried out in a similar manner.

Quantum Yield Determination for I-36

The method of Parker[102] was followed. The light source was found to emit 1.05 X 10^{15} photons per sec.. Ylid consumption as well as triphenylphosphine and azobenzene formation for the first 10 min., when absorption interference from azobenzene was negligible, were determined by glpc with authentic samples using octadecane as internal standard (Table V).

Irradiation of Ylid I-38

A 25 mM solution (110 ml) of ylid I-38 in benzene was irradiated through a pyrex filter for 3 hours. The photolysate was concentrated to 10 ml and analyzed by glpc. Comparison of the retention characteristics of the photolysate components with 2-ethyl-2,3-dihydroindole and 2-methyltetrahydroquinoline generated by photocyclization of o-butylphenyl azide[89] revealed these components were not formed ($< 0.1\%$) during irradiation of ylid I-38. Two components were detected (49%) in addition to triphenylphosphine and 2-butylaniline (50%) and were isolated from the photolysate by preparative glpc..

Calc. for $C_{20}H_{26}N_2$ 294(M^+); Found 294(M^+)

They were found to interconvert upon separate irradiation. and possessed UV max at 320 nm and 285 nm. By analogy with trans (λ_{max} 319 nm) and cis (λ_{max} 280 nm) azobenzene[107] these two compounds are considered to be trans and cis o,o'-dibutylazobenzenes.

Irradiation of Ylid I-39

Solutions (110 ml) of ylid I-39 (27 mM) in the solvents given in Table VII containing octadecane standard were each irradiated for 9 hours through a pyrex filter. The photolysate was concentrated to 10 ml and analyzed by glpc. Biphenyl, o-aminobiphenyl, carbazole, triphenylphosphine, and azobiphenyl were identified by mixed injection with authentic samples. Yields given in Table VII were calculated in the usual manner. The effect of alteration of purge gas in these experiments while keeping the reaction parameters unchanged is recorded in Table VIII.

Irradiation of 2-Aminobiphenyl with Triphenylphosphine

A 110 ml benzene solution of 2-aminobiphenyl (0.856 gm) and triphenylphosphine (1.336 gm) with octadecane as internal standard was irradiated for 6 hours with oxygen as purge gas. o-Aminobiphenyl remained unreacted buttriphenylphosphine was partially converted to triphenylphosphine oxide (46.8%).

Irradiation of Ylid I-36 in Various Purge Gas

A 110 ml benzene solution of 10 mM ylid I-36 was irradiated through a pyrex filter separately with dry helium and dry oxygen as purge gas. With dry helium as purge gas, azobenzene (94±5%) and triphenylphosphine (90±5%) were the only products formed. With dry oxygen as purge gas, the products formed were triphenylphosphine oxide (90±5%), carbazole (15±5%), aniline (5±2%), azobenzene (5±2%) nitrobenzene (trace) and nitrosobenzene (15±5%). Yields were calculated with octadecane as internal standard and authentic samples.

Thermolysis of Ylid I-36 with Purged Oxygen

A 50 ml benzene solution of ylid I-36 (0.34 gm) was refluxed overnight under anhydrous condition purged with dried oxygen (Anhydrous calcium chloride). Glpc analysis indicated ylid I-36 remained unreacted (octadecane as internal standard) and no aniline and/or triphenylphosphine and/or triphenylphosphine oxide were formed.

Irradiation of Diphenylamine

A 110 ml benzene solution of diphenylamine (0.5111 gm) and octadecane (0.4232 gm) (internal standard) was irradiated for 6 hours with oxygen as purge gas (to simulate our reaction condition for the irradiation of ylid I-36). Analysis of reaction mixture by gplc indicated formation of cabazole in 35% yield.

Irradiation of I-44 in presence of Phenyl Azide

A 110 ml benzene solution of ylid I-44 (1.0gm) and phenyl azide (0.8 gm) containing octadecane standard was irradiated for 6 hours through pyrex filter. Analysis of the concentrated photolysate by glpc indicated no asymmetric azobenzene or triphenylphosphine was formed. Azobenzene (40%) and aniline (< 1%) were formed. Ylid I-44 remained unreacted.

Thermolysis of p-tolyl Azide and Ylid I-36

A 100 ml benzene solution of ylid I-36 (1 gm) and p-tolyl azide (0.37 gm) were refluxed overnight under anhydrous condition. Glpc analysis indicated ylid I-36 remained unreacted (octadecane as internal standard).

Irradiation of p-tolyl Azide and Ylid I-36 Mixture

A 110 ml benzene solution of p-tolyl azide (0.37 gm) and ylid I-36 (1.0 gm) containing octadecane as standard was irradiated for 3 hours through a pyrex filter. The photolysate was concentrated to 10 ml and analyzed by glpc (Discussion).

Irradiation of I-46 and Phenyl Azide Mixture

A benzene solution (110 ml) of phenyl azide (0.40 gm) and ylid I-46 (1.05 gm) was irradiated for 3 hours through a pyrex filter. The photolysate was concentrated to 10 ml and analyzed by glpc (discussion).

Reaction of 2-Nitrosobiphenyl with Ylid I-39

Equimolar quantities of 2-nitrosobiphenyl and ylid I-20 were refluxed in benzene and the reaction followed by glpc. The products formed were azobiphenyl and triphenylphosphine oxide in 42% and 80% yield respectively. 2-Nitrosobiphenyl was prepared by the procedure of Havinga[110] m.p. 112-114°C (ethanol).

Irradiation of I-36 and I-46

A 110 ml benzene solution of I-36 (0.7 gm) and ylid I-46 (0.6 gm) was irradiated for 3 hours through a pyrex filter. The photolysate was concentrated for 10 ml and analyzed by glpc (discussion).

Irradiation of Methylazidoformate and I-36

A 110 ml benzene solution of methylazidoformate (0.3 gm) and I-36 (1.0 gm) was irradiated for 3 hours through a pyrex filter. The photolysate was concentrated to 10 ml and analyzed by glpc. I-44 and azobenzene were the only products formed.

Irradiation of Ylid I-48

A 110 ml ether solution of ylid I-48 (1 gm) containing octadecane standard was irradiated for 12 hours through a pyrex filter. The photolysate was concentrated to 10 ml and analyzed by glpc. Triphenylphosphine and imine I-50 were isolated by prep glpc. For I-50: calc. $C_{15}H_{13}N$ 195(M^+); Found 195(M^+). Acid hydrolysis of I-50 afforded benzaldehyde and benzylamine[109].

Condensation of Analine with Formaldehyde

Equimolar quantities of aniline and formaldehyde in benzene were refluxed azeotropically with a Soxhlet refluxer until the theoretical quantity of water had been formed. Upon evaporation of benzene, the residue was recrystallized from benzene-petroleum ether to give 75% yield of a trimer of I-53 as a white solid, m.p. 141-2°C. For I-53: Calc. for $C_{21}N_{21}N_3$ 315(M^+); Found 315(M^+)

Irradiation of Ylid I-54

An ether solution (110 ml) of ylid I-54 (1 gm) containing octadecane standard was irradiated for 12 hours through a pyrex filter. The photolysate was concentrated to 10 ml and analyzed by glpc. Products listed in Table X were identified by mixed injection with the authentic samples. The major products, I-55 and triphenylphosphine, were isolated by prep glpc. For I-55: calc. $C_{12}H_{21}N$ 179(M^+); Found 179(M^+).

Preparation of I-55

Equimolar quantities of cyclohexylamine and cyclohexanone in benzene were refluxed azeotropically with a

Soxhlet refluxer until the theoretical quantity of water had been separated out from benzene. Upon evaporation of benzene, the residue was a colorless oil b.p. 136-7°C/15 min. (70% yield). Lit. b.p. 136-7°C/15 min.[108].

Irradiation of Ylid I-49

A benzene solution (110 ml) of ylid I-49 (0.5 gm) containing octadecane standard was irradiated for 6 hours through a pyrex filter. The photolysate was concentrated to 10 ml and analyzed by glpc. Triphenylphosphine and N-phenylbenzophenone imine (I-58) were the only products formed. For I-58: Calc. $C_{19}H_{15}N$ 257(M^+); Found 257(M^+). The imine I-58 was identical to the condensation product of aniline and benzophenone, m.p. 112°C (lit. m.p. 110-2°C[109]).

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