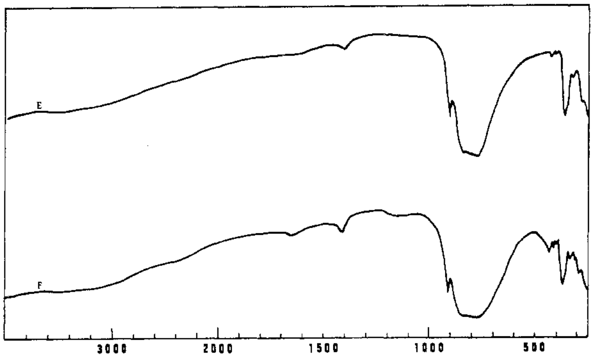

**Figure 2.** Infrared spectra (4000–250 cm$^{-1}$) for: (E) $Ge_3N_4$ prepared at 790 °C by the CVD process; (F) $Ge_3N_4$ prepared at 760 °C by the CVD process.

temperature. For a given ammonia–hydrogen mixture the $\beta$ phase was obtained at a higher temperature than the $\alpha$ phase. The $\beta$ phase can be prepared pure by reaction of ammonia and elementary germanium. Thus, oxygen is not necessary for the formation of either crystalline phase. The progressive increase in the percentage of $\beta$ phase with increasing deposition temperature suggests that the $\alpha$ and $\beta$ phases are two polymorphic varieties of germanic nitride, though we have verified the impossibility of the $\alpha$–$\beta$ transition at any temperature; this result confirms those obtained by Labbe[6] and by Bradley and co-workers.[4]

**Registry No.** $Ge_3N_4$, 12065-36-0.

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## Photoinduced Oxidation of Tertiary Arylphosphines

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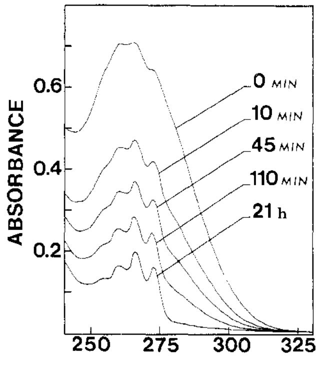

**Figure 1.** Electronic absorption spectral changes during irradiation with a fluorescent desk lamp of an $8.8 \times 10^{-5}$ M oxygen-saturated $CH_2Cl_2$ solution of triphenylphosphine.

Tertiary phosphines are an important class of ligands in inorganic and organometallic chemistry, in part due to their unique $\sigma$-donor and $\pi$-acceptor properties and their resistance to chemical transformation. Unlike trialkylphosphines, tertiary phosphines that contain at least one aryl group are not very sensitive toward autoxidation. Triphenylphosphine, for example, yields only a trace of its oxide when heated under an oxygen atmosphere in benzene.[1] Under similar conditions, most trialkylphosphines readily undergo a free-radical chain autoxidation process yielding as principal products the corresponding phosphine oxides and phosphinate esters.[1] Triarylphosphines can be oxidized by molecular oxygen, however, by treatment with a radical initiator, and triphenylphosphine yields its oxide exclusively under these conditions.[1]

In the course of our investigations into the photochemical properties of some transition metal–phosphine complexes, we have discovered that uncoordinated arylphosphines are readily oxidized by molecular oxygen when irradiated with ultraviolet light or with fluorescent room light. Since this observation is of importance to workers investigating the photochemical properties of phosphine complexes, we have examined these photoreactions in some detail and report our results herein. Although the photoinduced oxidation of triphenylphosphine to triphenylphosphine oxide has been briefly mentioned in the literature,[2,3] quantum yield data have not been presented and the high photosensitivity of arylphosphines in the presence of oxygen has apparently not been generally appreciated.

### Experimental Section

Triphenylphosphine was obtained from Aldrich Chemical Co. and was recrystallized from EtOH before use. $PMePh_2$, $PEtPh_2$, $PMe_2Ph$, and $PEt_2Ph$ were synthesized from $PPh_2Cl$ and $PPhCl_2$ and the appropriate Grignard reagent following an adaptation of the literature procedure.[4] Methyldiphenylphosphine oxide was prepared by heating $PMePh_2$ with ethylene carbonate[5] and was characterized by its melting point (110–111 °C[6]), its infrared spectrum ($\nu_{P=O}$ 1122 cm$^{-1}$), and its $^1H$ NMR spectrum ($\delta$ 1.95 and 2.16[7]). A low-pressure Hg-arc lamp (254 nm), a Hanovia 450-W medium-pressure Hg-arc lamp equipped with Corning 0-52 and 7-37 glass filters (366 nm), an Ultraviolet Products B-100A lamp (366 nm), and a Sylvania F40/CW 40-W fluorescent desk lamp were used as the irradiation sources for the photochemical studies. Quantum yields were measured at 254 nm in oxygen-saturated $CH_2Cl_2$ solutions using ferrioxalate actinometry ($I = 2.2 \times 10^{-7}$ einstein/min). Electronic absorption spectral changes were monitored with a Cary 17 spectrophotometer, infrared spectral changes were recorded on a Perkin-Elmer 621 grating infrared spectrophotometer, and $^{31}P$ NMR spectra were recorded on a JEOL PS-100-FT Fourier-transform NMR spectrometer. Reported chemical shifts are relative to external $H_3PO_4$.

### Results and Discussion

Photolysis of an $8.8 \times 10^{-5}$ M oxygen-saturated $CH_2Cl_2$ solution of $PPh_3$ with a fluorescent desk lamp results in the electronic absorption spectral changes shown in Figure 1. As the irradiation proceeds, the intense band centered at 270 nm steadily decreases in intensity and the final spectrum obtained is identical with that of triphenylphosphine oxide. In the infrared spectral region the $PPh_3$ band at 1080 cm$^{-1}$ decreases in intensity with increased irradiation time, and $Ph_3PO$ bands

**Table I.** Oxidation Quantum Yields of Tertiary Arylphosphines

| Tertiary phosphine | Quantum yield[a] | Tertiary phosphine | Quantum yield[a] |
|---|---|---|---|
| $PPh_3$ | 3.3 | $PEtPh_2$ | 3.6 |
| $PMePh_2$ | 5.4 | $PEt_2Ph$ | 4.5 |
| $PMe_2Ph$ | 4.9 | | |

[a] Measured in oxygen-saturated $CH_2Cl_2$ solution using 254-nm irradiation; values given are accurate to within ±10%.

simultaneously appear and increase at 1117 and 1188 $cm^{-1}$. The photoreaction can be induced with 254, 313, and 366 nm or with fluorescent room light irradiation. The 254-nm quantum yield of disappearance of $PPh_3$ is $3.3 \pm 0.3$. The mixed (alkyl–aryl)phosphines $PMePh_2$, $PEtPh_2$, $PMe_2Ph$, and $PEt_2Ph$ are also photosensitive in the presence of oxygen and give uv and ir spectral changes similar to those obtained for $PPh_3$. The only product that we were able to isolate from irradiated $PPh_3$ solutions was $Ph_3PO$, and the lack of P–O–R vibrations in the infrared spectra of irradiated solutions of the other phenylphosphines suggests that the corresponding oxide is the major product in each case. Further, the $^{31}P$ NMR spectra of irradiated $CDCl_3$ solutions of $PPh_3$, $PMePh_2$, $PMe_2Ph$, and $PEtPh_2$ each showed only a single resonance with chemical shifts of 30.1, 30.0, 33.7, and 34.3 ppm, respectively. These shifts are similar to those reported[8] for the corresponding oxides, and the $^{31}P$ NMR spectrum of an authentic sample of $MePh_2PO$ in $CDCl_3$ was identical with the spectrum of the irradiated $PMePh_2$ solution.

The 254-nm quantum yields for the phosphines studied (Table I) are all greater than 3 and imply that the oxidation proceeds through a free-radical chain mechanism. The photoactive excited state of the arylphosphines most likely results from the intense $n \rightarrow \pi^*$ transition[9] centered around 260 nm, and various chain initiation pathways from this excitation can be proposed. A discussion of the detailed initiation and propagation mechanisms, however, must await further experimentation.

The high quantum yield oxidations reported herein and our previous findings[10,11] that many triphenylphosphine complexes are photosensitive only when irradiated in the presence of $O_2$ suggest that workers investigating the photochemical and thermal properties of tertiary phosphine complexes should seriously consider the possibility of photoinduced oxidation. It is especially important that kinetic and mechanistic studies of complexes that dissociate tertiary phosphines or studies employing an excess of tertiary phosphines be protected either from oxygen or from uv light. Ordinary fluorescent room light is of sufficient energy to induce the oxidation of the phosphines examined in this work.

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**Registry No.** $PPh_3$, 603-35-0; $PMePh_2$, 1486-28-8; $PMe_2Ph$, 672-66-2; $PEtPh_2$, 607-01-2; $PEt_2Ph$, 1605-53-4.

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# Charge Distribution and Carbon-13 Nuclear Magnetic Resonance Shifts in Tricarbonyl(dienyl)iron Cations

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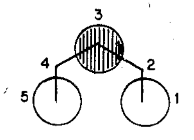
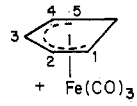
Tricarbonyl(dienyl)iron cations in which the dienyl ligand possesses a "U" conformation are unusually stable.[2] This stability can be understood in terms of a frontier orbital model in which an occupied orbital on iron donates electrons to the nonbonding $\pi$ LUMO of a dienyl cation ($\psi_{NB}$).[3,4] $^{13}C$ NMR shifts show uncomplexed cyclohexadienyl(benzenium) cations are highly electron deficient only at carbons 1, 3, and 5,[5] as expected if $\psi_{NB}$ is unoccupied. Electron donation to $\psi_{NB}$ in iron-complexed cations ought to reduce or even reverse the charge alternation found in cyclohexadienyl cations.



$\psi_{NB}$

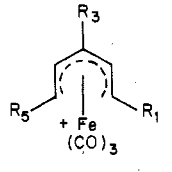
$^{13}C$ NMR chemical shifts for three tricarbonyl(cyclohexadienyl)iron cations (e.g., **1**) have been published by Shubin et al.[6] The relative importance of the several factors which determine NMR shifts of carbons bound to transition metals is not yet known.[7] Thus, application of the charge density–$^{13}C$ chemical shift correlation, which is well recognized for uncomplexed conjugated systems,[8] in the absence of independent evidence for its validity would be risky. Shubin et al. cautiously concluded that the $Fe(CO)_3$ group participates effectively in delocalization of the positive charge.



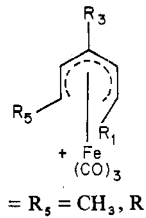
**1**

Recently, however, Hoffmann and Hofmann have calculated a charge distribution for cation **1** using the extended Hückel (E-H) method.[9] While the E-H atomic charges are quantitatively unreliable, the calculated charge distribution *pattern* should be valid. Carbons 1, 3, and 5 are predicted to be electron *rich* relative to carbons 2 and 4 with 1 and 5 bearing the largest net negative charges. There is a striking correlation between these results and the chemical shift data for **1**: $C_{1,5}$ at 62.8 ppm, $C_3$ at 87.8 ppm, and $C_{2,4}$ at 100.8 ppm.[10] The higher the calculated electron density is, the greater is the observed shielding.

The correlation between E-H charge density and $^{13}C$ chemical shift is not unique to cyclohexadienyl ions. $^{13}C$ NMR data for a series of acyclic cations **2–6** are presented in Table I.[11,12] The $^{1}J_{C-H}$ values for the dienyl carbons fall (within



**2**, $R_1 = CH_3$, $R_3 = R_5 = H$
**3**, $R_1 = R_5 = CH_3$, $R_3 = H$
**5**, $R_1 = R_3 = R_5 = CH_3$



**4**, $R_1 = R_5 = CH_3$, $R_3 = H$
**6**, $R_1 = R_3 = R_5 = CH_3$