Y = morpholino, X = CO₂Me	pressure	53%	0%	0%
	heat	0%	29%	23%
Y = piperidino, X = CN	pressure	90%	0%	0%
	heat	3%	10%	20%

ware equipment and can be performed on a 10–20-g scale. The effect of increased substitution to inhibit the cycloaddition reaction became apparent in the attempted reaction of ethyl sorbate with the pyrrolidine enamine of isobutyraldehyde (entry 4). The failure of ethyl cyclohexadienecarboxylate to react with the pyrrolidine enamine of propionaldehyde and isobutryaldehyde (entry 7 and 8) also might reflect the unfavorable electronic effect of an α-substituent.

For the reaction of dienamines with enoic esters, ene nitriles, and enones (i.e., conjugated acceptors) again it was found that the cycloaddition proceeded well at room temperature and generally in higher yield and shorter reaction time than the thermally induced process. In the pressure range studied, similar steric and/or electronic effects of the added β-substituent in the conjugate acceptor were found; i.e., in going from pent-3-en-2-one (entry 12) to mesityl oxide (entry 13) the reaction was inhibited. Of particular interest was the finding that under pressure the reaction of isophorone dienamine with methyl acrylate (entry 19) and with acrylonitrile (entry 20) yielded only the Diels–Alder type adduct. These same reactions have been studied thermally and found to give different product distributions.[6] Thus, the use of high pressure can effect a change in the course of a reaction as well as provide product specificity.

A sensitivity of the cycloaddition to pressure was found for entry 11; at 9.8 kbar pressure none of the desired product was obtained but at 13.9 kbar pressure the product was obtained in 70% yield. This pressure dependency warrants further study, especially in those cases where no product was obtained.

The last four examples (entries 21–24) involve the preparation of hindered systems. It was found that by double activation of the conjugate acceptor it was possible to overcome the deleterious effect of two β-substituents. The reaction of 1-pyrrolidino-1,3-butadiene with ethyl 2-cyano-3-methyl-2-octenoate can, in fact, be done at atmospheric pressure and room temperature. However, this cyano ester failed to react with 1-pyrrolidino-1,3-pentadiene even at 80° for a prolonged period. This latter reaction was effected in quantitative yield at 20 kbar pressure in 10 min. Attempts to purify the products of the last four reactions by preparative vpc or Kugelrohr distillation at reduced pressure resulted in retrocycloaddition.

The use of high pressure is extremely valuable in those cases where steric hindrance to reaction or thermal instability of a reactant precludes the use of conventional means to accelerate sluggish reactions. Furthermore, in the pressure reaction the amino compound

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can be isolated if so desired; this is not possible for most thermal reactions.[7]

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A Photoelectron Spectroscopic Study of Polyphosphines. The Question of pπ:dπ Bonding

Sir:

Polyphosphines have been the subject of much recent attention.[1] Such compounds, unlike their monophosphine analogs, show intense uv absorption, and it has been generally believed[2,3] that this is due to the delocalization of phosphorus lone pair electrons into higher orbitals of appropriate symmetry of juxtaposed phosphorus atoms. This model has, however, been questioned both on structural grounds[4] and from consideration of electronegativity.[5] Here we wish to report some preliminary results of a study of polyphosphines by photoelectron spectroscopy (pes) which have a bearing on this problem.

The observation of more than one peak in the phosphorus lone pair region for a cyclopolyphosphine can be attributed to interactions between the phosphorus lone pairs. In the case of $(CF_3P)_4$ (1) the molecular symmetry is known[6] to be D_{2d}. Hence the MO's derived from the lone pairs are of symmetry B_2, E, and A_1, having the forms indicated in Figure 1. In A_1, all four nearest neighbor interactions are antibonding, in B_2 all are bonding, while in E all such interactions are nonbonding. The order of increasing orbital energy, and so of decreasing ionization potential, should therefore be $B_2 < E < A_1$. Furthermore, the transannular interactions in A_1 and B_2 are bonding but in E antibonding; the A_1–E separation should therefore be less than the E–B_2 one. The first three ionization potentials (I_1, I_2, I_3) follow this pattern and can be assigned respec-

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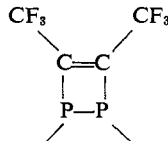(3) L. R. Grant and A. B. Burg, J. Amer. Chem. Soc., 84, 1835 (1962).
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Table I. Pes Ionization Potential[a] Data for Polyphosphines and $(CF_3)_3P$

Compound	No.	Lone pair IP's	Mean lone pair IP	P–P	P–C	Other
$(CF_3P)_4$	1	10.18, 10.58, 12.38	10.93	12.89	13.50	
$(CF_3)_4P_2$ (trans)[b]	2	10.71, 12.11	11.44	13.09	13.49	
$(CF_3)_3P$	3	11.70	11.70		13.52	
$(CF_3P)_5$	4	9.71, 10.16, 10.70, 11.21, 11.73	10.70	12.32, 12.67	13.89	
(structure 5)	5	10.97	10.97	12.62	13.78, 14.11	C=C, 12.14
$(CF_3)_2PP(CH_3)_2$	6	9.37, 10.38	9.88	11.64	11.64 13.29	
$(CH_3)_4P_2$ (trans)[b]	7	7.88, 9.54	8.71	10.33	11.22, 11.33	

[a] Vertical ionization potential in electron volts. [b] Similar data were obtained for the gauche rotamer. See ref 7.
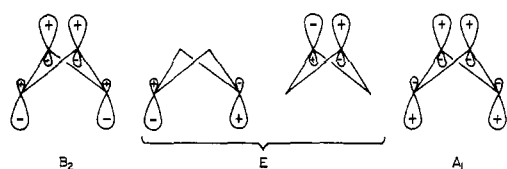
Figure 1. MO's derived by mutual interaction of the phosphorus lone pair AO's in $(PCF_3)_4$.

tively to A_1, E, and B_2 (Figure 2a). The observed ionization potentials lead to the following interaction parameters: β_{12}, 1.10 eV; β_{13}, 0.90 eV. Note also that I_2 is more intense than I_1 or I_3, as would be expected since the E level is doubly degenerate.

The next two pes peaks (I_4, I_5) can be assigned to ionization of P–P and P–C σ-bonds, respectively, by comparison with the corresponding peaks in 2[7] and 3 (Table I).

Since the cyclopentaphosphine, $(CF_3P)_5$ (4), is devoid of symmetry,[8] five nondegenerate lone pair ionizations are anticipated. The first five pes peaks of 4 (Figure 2b) are therefore assigned to phosphorus lone pair ionizations. Arguing by analogy with the pes of 1, 2, and 3 (Table I), the most reasonable assignment for peak I_8 (13.89 eV) is ionization of the P–C σ-bond. In turn this implies that peaks I_6 and I_7 (12.32 and 12.67 eV) are due to ionization of the P–P σ-bonds. The observation of two such peaks is consistent with the wide scatter of P–P bond distances in 4.[8]

Arguments analogous to the foregoing have been used to assign the phosphorus lone pair and the P–P and P–C σ-bond ionizations in 5 (Table I and Figure 2c). The remaining low energy peak (I_2, 12.14 eV) is therefore ascribed to ionization of the carbon–carbon double bond. The observation of two peaks (I_4 and I_5) in the P–C σ-bond region is presumably due to the fact that 5 contains both endo- and exocyclic P–C bonds.

The pes bands of the hybrid diphosphine 6 can be assigned unambiguously by comparison with those of the two corresponding symmetrical diphosphines 2 and 7 (Table I).

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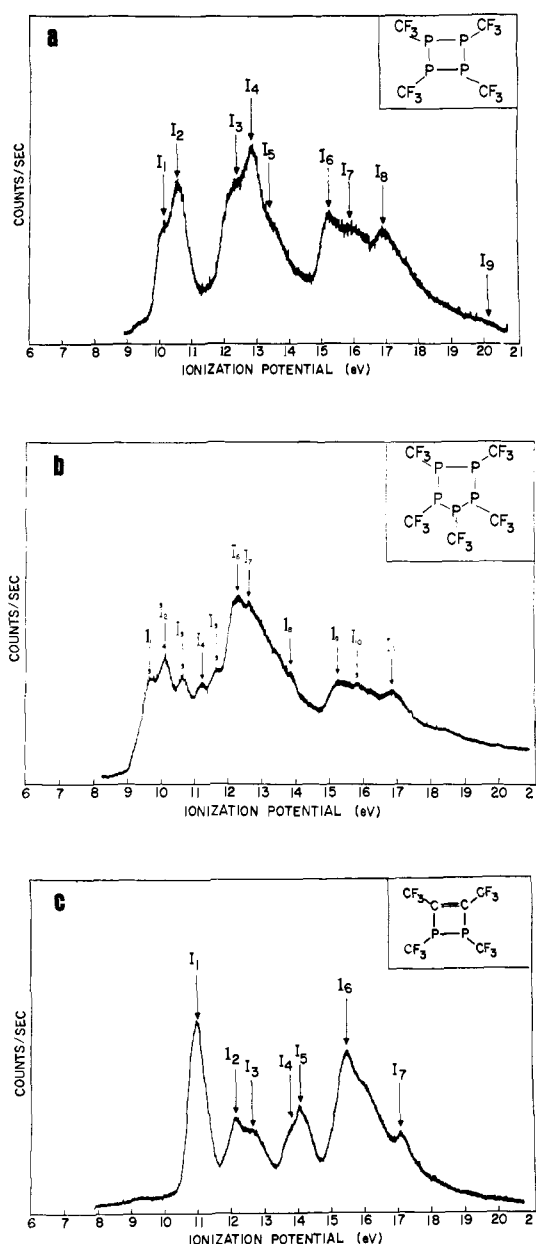
Figure 2. He(I) photoelectron spectra of (a) $(PCF_3)_4$ (1), (b) $(PCF_3)_5$ (4), and (c) $(F_3C)_2C_2P_2(CF_3)_2$ (5).

Communications to the Editor

Since the interactions between the phosphorus lone pair AO's do not alter their total energy, the average lone pair binding energy in a polyphosphine should be equal to *minus* the average of the corresponding IP's. The values found in this way (allowing for the degeneracy of I_2 in **1**) are shown in Table I. It will be seen that those for **1-4** can be quite well explained in terms of a simple inductive effect by the CF_3 groups. Thus the average values rise in the order $(1 \sim 4) < 2 < 3$, and while extrapolation of the values for **1**, **2**, and **4** leads to an estimate (12.06 eV) for **3** which is larger than that (11.70 eV) observed, the difference is small and could very well be due to increased bond angles at phosphorus, and consequent increase in lone pair s character, in **3**. If $p\pi:d\pi$ bonding were important, it would increase the lone pair binding energy in **1**, **2**, and **4** relative to **3**. Our results therefore indicate that such bonding must be relatively unimportant.

The mean lone pair binding energies of the other compounds listed in Table I also seem to follow a simple inductive pattern. Thus the values for **1** and **5** are almost identical, as would be expected on this basis, and that for **6** is close to the mean (10.07 eV) of the values for **2** and **7**. It is interesting that only one lone pair signal was obtained from **5**. This could be due to orthogonality of the two phosphorus lone pair orbitals (P_1 and P_3), combined with a negligible coupling to the C=C π MO. Alternatively the splitting by mutual interaction between P_1 and P_2 into a lower antisymmetric (to C_2) combination ($P_1 + P_2$) and a higher symmetric one ($P_1 - P_2$) could be just balanced by an equal interaction between the former and the antisymmetric bonding C=C π MO.

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Nonlinear Quenching and Variable Excited State Lifetimes in the Photochemistry of Mixed Chromophores[1]

Sir:

The classic Stern–Volmer (S-V) quenching technique[2] remains the simplest, most widely used method of determining excited state lifetimes when a single quenchable excited state is involved. If two or more excited states of a compound are reactive and/or are quenched, S-V quenching plots usually curve. Extracting excited state lifetimes in such cases is nontrivial, since both the initial and final slopes of such curved plots are composite functions of the decay kinetics of both states.[3-5]

Only one paper has been published exemplifying such complications, in compounds displaying irreversible singlet → triplet intersystem crossing.[6]

Excitation transfer within "bichromophoric" compounds[7] is attracting increased attention as photochemists expand their studies to polyfunctional systems. On the other hand, mixtures of different molecules with similar absorbances have received little, if any, quantitative study, despite the excellent possibility that this situation may be widespread in biological and environmental systems. Both mixtures and bichromophores are obvious candidates for the complicated quenching kinetics which can attend the presence of more than one quenchable excited state. We have recently described a nonconjugated diketone in which excitation is rapidly equilibrated between the lowest triplets of both chromophores.[8] In such cases S-V quenching plots are linear (slopes proportional to equilibrium lifetimes) at quencher concentrations sufficiently low that thermal interconversion of the states is not impeded.[5] We now report the first example of nonlinear quenching due to interference with excited state interconversion in systems containing two independent absorbing chromophores.

We have studied various combinations of the benzoyl and p-methoxybenzoyl (anisoyl) chromophores, either as mixtures of two ketones or as α,ω-diaroylalkanes. These two chromophores were chosen since they have similar triplet excitation energies[6] and very different triplet lifetimes.[9] For example, with mixtures of nonanophenone (NB) and p-methoxynonanophenone (NA), 313-nm[10] irradiation of degassed benzene solutions produces both acetophenone and p-methoxyacetophenone, indicating that each chromophore undergoes Norrish type II photoelimination.[11] Relative quantum yields of these products in the presence of various concentrations of 2,5-dimethyl-2,4-hexadiene (an efficient quencher of triplet ketones)[12,13] were determined by glc analysis following the usual parallel irradiation of samples.[12] Figures 1 and 2 exemplify the kind of S-V quenching plots obtained in such systems. Figure 1 plots acetophenone formation from NB both in the absence and presence of 0.01 M NA. The measured $k_q\tau$ value for nonanophenone alone is 31 M^{-1},[14,15]

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