# A Kinetic Study of the Reaction of Diazoalkanes with Triphenylphosphine: Structure and Reactivity in a Biphilic Process

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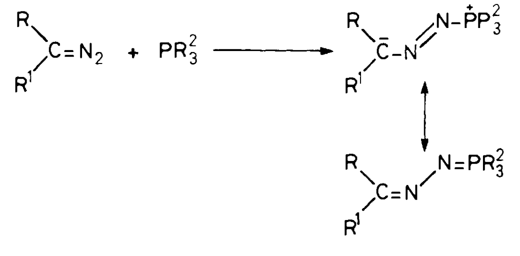
Second-order rate coefficients and activation parameters are reported for the reaction in solution of triphenylphosphine with a series of diazoalkanes ($Ar_2CN_2$) having two aromatic groups attached to the diazo-carbon atom, 9-diazofluorene (DAF), 5-diazo-5*H*-dibenzo[*a,d*]cycloheptene (DBSE), its 10,11-dihydro analogue (DBSA), and diazodiphenylmethane (DDM). Although the product phosphazine $Ar_2CNNPPh_3$ arises formally by nucleophilic attack of phosphorus on the terminal nitrogen atom of the diazoalkane, the pattern of reactivity approximates to that for proton transfer from acetic acid to the diazoalkane under similar conditions, highlighting the biphilic nature of the reaction. The results can be rationalised in terms of qualitative FMO theory taking into account both HOMO($Ph_3P$)–LUMO ($Ar_2CN_2$) and HOMO($Ar_2CN_2$)–LUMO ($Ph_3P$) interactions. This is lent qualified support by MNDO calculations on $Ar_2CN_2$ based on molecular parameters from the *X*-ray crystal structure of DAF itself and of the ketones corresponding to DBSE, DBSA, and DDM.

The reactivity of DDM and the effect of 4,4′-disubstitution by $CH_3O$–, $CH_3$–, and Cl–, which gives rise to a U-shaped Hammett ρσ correlation, is not easily interpreted within the FMO framework. Conformational changes which affect the interacting orbitals as the reactants are transformed into transition states offer an alternative interpretation.

Diazo-compounds react quantitatively with phosphines to form 1:1 adducts, usually referred to as phosphazines or phosphinazines and shown in two limiting structures in Scheme 1.[1] These products are usually thermally stable but can be decomposed at high temperatures and in the presence of copper catalysts[2] or by electrochemical means.[3] Their formation can be considered to represent a nucleophilic attack of the phosphine on the terminal nitrogen of the diazo-function,[4] and this is implied by the dipolar limiting structure of the phosphazine. The alternative limiting representation of the product uses d orbitals on phosphorus, and suggests that the reaction is more correctly represented as a biphilic process[5] in which both reaction partners behave concurrently as electrophile and nucleophile with the formation of two bonds one of σ- and one of π-type. The interaction of phosphine and diazo-compounds thus represents a wholly organic analogue of the well-known phosphine–transition metal binding,[6] and represents a relatively simple type of organic reaction in which two bonds are formed synchronously.

In this paper we report kinetic results for the reaction of triphenylphosphine with a group of structurally, quite closely, related diazoalkanes ($Ar_2CN_2$); all carry two aromatic groups attached to the diazo-carbon atom but have markedly different abilities to delocalise positive and negative charge. The pattern of kinetic behaviour is rather unexpected, and we interpret it qualitatively in terms of Frontier Molecular Orbital (FMO) theory.[7] Attempts to support the FMO rationalisation by MNDO calculations are also described.



**Scheme 1.**

## Results and Discussion

*Kinetic Form of the Reaction.*—Reactions were carried out in homogeneous solution in acetonitrile with the triphenylphosphine in large excess over the diazoalkane. Preparative reactions were carried out and the product phosphazine isolated by crystallisation in approximately quantitative yield. For the kinetic experiments, reactions were followed spectrophotometrically and final spectra were in good agreement with predictions for quantitative reaction. Reactions were followed either by the disappearance of the visible absorption of the diazoalkane or, more usually, by the appearance of the phosphazine absorption between 350 and 400 nm. First-order rate coefficients, $k_{obs}$, were obtained from absorbance data collected over at least 75% of reaction and were evaluated from the integrated rate equation using a least-squares procedure (correlation coefficients always >0.999). Table 1 shows results for the four diazoalkanes investigated, 9-diazofluorene (DAF) (**1**), 5-diazo-5*H*-dibenzo[*a,d*]cycloheptene (DESE) (**2**), 5-diazo-10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene (DBSA) (**3**) and diazodiphenylmethane (DDM) (**4**). In addition, the effect of 4,4′-disubstitution on the reactivity of DDM was investigated at 30 °C, and the relative reactivities are given in Table 2.

It is apparent from the values of $k_{obs}$ in Table 1 that they are proportional to the phosphine concentration. Second-order rate constants, $k_2 = k_{obs}/[PPh_3]$, show fairly small standard deviations, and this confirms the findings of Goetz and Juds[8] who demonstrated a similar kinetic form in benzene solution for the reaction of DAF with $PPh_3$. In the present experiments there was no evidence of formation of 9,9′-bifluorenylidene in a competitive process as had been observed in benzene. It is noteworthy, however, that $k_2$ in benzene at 35 °C was reported to be $2.3 \times 10^{-4}$ compared to a value of $8.8 \times 10^{-4}$ $dm^3$ $mol^{-1}$ $s^{-1}$ in $CH_3CN$ (calculated from the activation parameters in Table 1). This modest acceleration on substantially changing

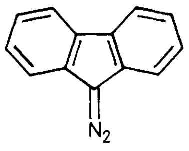
**Table 1.** Kinetics of the reaction between diazoalkanes and triphenylphosphine in acetonitrile solution.[a]

| Diazoalkane | $[Ph_3P]/10^{-2}$ mol dm$^{-3}$ | $k_{obs}/10^{-5}$ s$^{-1}$ 30 °C | 40 °C | 50 °C | $E_a$/kcal mol$^{-1}$ | $\Delta S^{\ddagger}$/cal K$^{-1}$ mol$^{-1}$ |
|---|---|---|---|---|---|---|
| DAF | 3.82 | 2.15 | 4.78 | 9.45 | | |
| | 7.63 | 4.10 | 9.05 | 17.8 | | |
| | 11.5 | 6.55 | 14.0 | 26.7 | | |
| | 19.1 | 11.3 | 23.8 | 47.0 | | |
| | $k_2/10^{-4}$ dm$^3$ mol$^{-1}$ s$^{-1}$ | 5.65 | 12.3 | 24.0 | 14.0 | −29.2 |
| | SD | ±0.22 | ±0.30 | ±0.81 | | ±0.3 |
| DDM | 3.82 | 12.4 | 23.2 | 39.5 | | |
| | 7.63 | 24.5 | 45.3 | 80.0 | | |
| | 11.5 | 35.7 | 66.7 | 121.7 | | |
| | 19.1 | 61.5 | 113.5 | 200.0 | | |
| | $k_2/10^{-4}$ dm$^3$ mol$^{-1}$ s$^{-1}$ | 32.0 | 59.4 | 104.7 | 11.5 | −34.1 |
| | SD | ±0.62 | ±1.1 | ±0.10 | | ±0.2 |
| DBSE | 3.82 | 16.7 | 38.3 | 57.5 | | |
| | 7.63 | 32.8 | 69.2 | 120.0 | | |
| | 11.5 | 45.0 | 109.7 | 166.7 | | |
| | 19.1 | 65.5 | 166.7 | 265.0 | | |
| | $k_2/10^{-4}$ dm$^3$ mol$^{-1}$ s$^{-1}$ | 40.0 | 93.4 | 147.9 | 12.7 | −29.6 |
| | SD | ±4.3 | ±5.7 | ±7.9 | | ±0.5 |
| DBSA | 3.82 | 1.87 | 5.05 | 7.33 | | |
| | 7.63 | 3.45 | 8.50 | 12.58 | | |
| | 11.5 | 4.93 | 12.23 | 19.17 | | |
| | 19.1 | 7.60 | — | 30.7 | | |
| | $k_2/10^{-4}$ dm$^3$ mol$^{-1}$ s$^{-1}$ | 4.42 | 11.7 | 17.1 | 13.1 | −32.6 |
| | SD | ±0.39 | ±1.4 | ±1.4 | | ±0.6 |

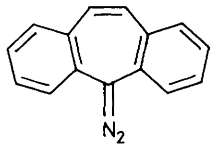
[a] 1 cal = 4.184 J.

**Table 2.** Relative reactivities of 4,4′-disubstituted diazodiphenylmethanes towards triphenylphosphine in acetonitrile solution at 30 °C.

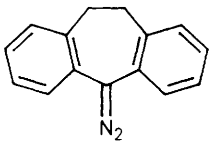
| Substituent | | $k_{rel}$ |
|---|---|---|
| **(4a)** | H | (1.00) |
| **(4b)** | Cl | 5.9 |
| **(4c)** | $CH_3$ | 1.3 |
| **(4d)** | $CH_3O$ | 2.1 |



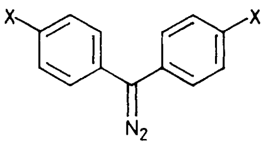
**(1)**: DAF



**(2)**: DBSE



**(3)**: DBSA



**(4)**

a; X=H (DDM)
b; X=Cl
c; X=$CH_3$
d; X=$CH_3O$

the solvent polarity suggests that there is little charge development in the transition state.

*Structural Effects on the Reactivity of Diazoalkanes.*—Two significant features emerge from the results in Table 1. The first is that the range of reactivity is remarkably small, less than one power of ten at any temperature. (This is in part a consequence of compensating changes in activation energy and entropy Table 1); for example DDM which has the lowest $E_a$ has the most negative $\Delta S^{\ddagger}$, and DAF with the highest $E_a$ has the least negative $\Delta S^{\ddagger}$. The variation in entropies of activation are, however, quite small, but are most negative in those diazoalkanes (DDM and DBSA) where conformational change is easiest.

The second notable feature is that the reactivity sequence of the diazoalkanes is DBSA < DAF < DDM < DBSE. This is roughly the reverse of what is expected if the reaction were simply nucleophilic attack of phosphorus on the terminal nitrogen of the diazoalkane; for example, the negative charge developing on the diazo-carbon atom in the transition state would be expected to be much better stabilised by the fluorenyl system of DAF with its cyclopentadienyl moiety than by the dibenzotropylium structure of DBSE. Indeed, the sequence of reactivity is quite similar to that obtained by measuring the rates of reaction of the diazoalkanes with acetic acid in $CH_3CN$ solution (Table 3). Here $k_{rel}$ is the relative reactivity of the diazoalkane determined from the second-order rate coefficients at 30 °C obtained in experiments in which a tenfold and twentyfold excess of the acid was added to the diazoalkane, the disappearance of which was followed spectrophotometrically.

The interpretation of small changes in reactivity is, we recognise, fraught with difficulty. This is particularly the case here where the steric situation in the transition states for

**Table 3.** Relative reactivities of diazoalkanes (0.01 mol dm$^{-3}$) towards acetic acid (0.1 mol dm$^{-3}$) in acetonitrile solution at 30 °C.

| Diazoalkane | $k_{rel}$ |
|---|---|
| DAF | (1.00) |
| DBSA | 2.5 |
| DDM | 7.7 |
| DBSE | 450 |

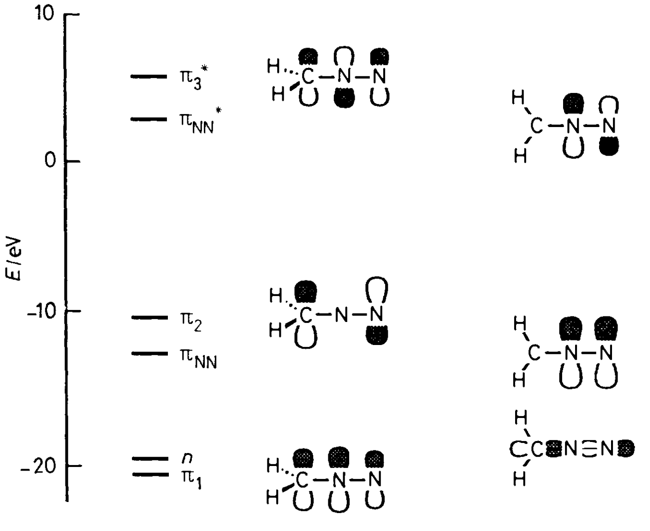


**Figure 1.** Schematic high energy orbitals of diazomethane (adapted from Ref. 11).

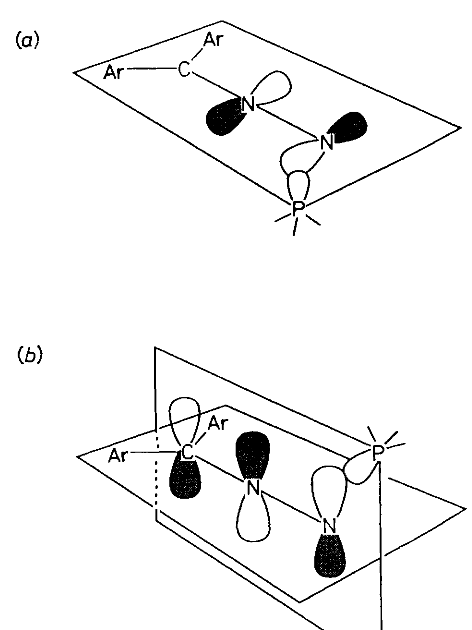


**Figure 2.** Trajectories for attack of phosphines on diazoalkanes.

phosphine attack on the four diazoalkane structures is likely to vary (see below). Steric effects have indeed been claimed to be important in phosphazine formation.[2a]

One possible interpretation of the present results is that, at the transition state, a π-type interaction between the diazo-compound (donor) and $PPh_3$ (acceptor) occurs as a consequence of the trajectory of the approach of the reagents and/or the diffuse nature of the orbitals employed (2p on N; 3d on P). We discount this since we believe that the more effective σ-overlap between N and P is likely to be well developed and thus an important factor in lowering the energy of the transition structure. Instead, the narrow range of reactivity leads us to an interpretation in terms of a balance between opposing interactions, in other words, a biphilic interaction of diazoalkane and phosphine. In this respect the present reaction is analogous to Type II of the classification of 1,3-dipolar cycloaddition reactions introduced by Sustmann, Huisgen and their co-workers.[9] Electronic effects of the diazoalkane structure which favour attack by the nucleophilic phosphorus will disfavour the simultaneous back-donation of electron density from the diazoalkane moiety to the phosphine and *vice versa*.

A simple way of considering the reactivity pattern is in terms of the interaction of the frontier orbitals of the reactants, considering both HOMO($PPh_3$)–LUMO($Ar_2CN_2$) and HOMO($Ar_2CN_2$)–LUMO($PPh_3$). Similar treatments have been used to handle the cycloaddition of carbenes to alkenes.[10] In both cases two σ-bonds are being formed concertedly but not necessarily synchronously. The same consideration could apply to phosphazine formation, although the perfect synchronisation of generation of the σ- and π-bond seems more likely in this case since both are formed between the same pair of atoms. The relevant molecular orbitals for diazomethane (which also forms a phosphazine with $PPh_3$) are shown schematically in Figure 1, together with the other orbitals of π-symmetry.[11] It can be seen that the orbitals fall into two categories, those of $B_1$ symmetry (in $C_{2v}$) which includes the HOMO and those of $B_2$ symmetry, representing π-type orbitals with lobes lying in the nuclear plane and including the LUMO. For planar molecules it is to be expected that on replacement of the hydrogen atoms in $CH_2N_2$ by groups having π-orbitals, conjugation will be with the diazo-group π orbitals of $B_1$-symmetry and this will lead to either an increase or decrease in the energies of $\pi_2$ and $\pi_3$* in Figure 1. To a first approximation, the energies of the π-orbitals of $B_2$ symmetry should be unaffected.

The pattern of results can thus be interpreted according to the usual FMO prescription in terms of orbital energies as follows. Interaction of the HOMO of triphenylphosphine, essentially the phosphorus lone pair, is with the unoccupied $\pi^*_{NN}$-orbital as shown in Figure 2(*a*). This interaction might be expected to be roughly invariant with diazoalkane structure. Simultaneously, the HOMO of the diazoalkane, of $B_1$-symmetry and, thus, structurally dependent, interacts with the d-orbital on phosphorus. The rate variation, on this explanation, arises largely from this latter interaction, specifically the energy of the diazoalkane HOMO. Consequently the reactivity of the diazoalkanes towards triphenylphosphine should parallel that towards simple electrophiles as exemplified by proton transfer.

Such a facile, qualitative rationalisation ignores a number of important features. The diazoalkanes studied here are not all planar; only DAF is flat, the other three have their α-aromatic groups tilted at substantial angles from the plane defined by the CNN moiety and the two *ipso*-carbon atoms (see below). Moreover, the barrier to rotation of the aromatic groups is variable, probably being lowest in the case of DDM so that the molecular conformation is least constrained in this case. The three compounds DAF, DBSE, and DBSA, thus, represent a more homogeneous group for purposes of structure–reactivity correlation.

The qualitative rationalisation also ignores the fact that extended conjugation can so lower the energy of orbitals of $B_1$-symmetry that the diazoalkane LUMO becomes $\pi_3$* rather than $\pi^*_{NN}$ as in $CH_2N_2$. The primary HOMO($PPh_3$)–LUMO($Ar_2CN_2$) interaction would then imply approach of the nucleophilic phosphorus in the mirror plane ($\sigma_v$ in $C_{2v}$) of the diazo group [Figure 2(*b*)]. Such an approach seems less likely

**Table 4.** Frontier-orbital energies/eV of diazoalkanes calculated by MNDO.[a]

| Diazoalkane | $E_{HOMO}$ | $E_{LUMO}$ | $E(\pi^*_{NN})$ |
|---|---|---|---|
| DAF | −8.153 | −0.704 | +0.010 |
| DBSA | −8.122 | −0.208 | 0.381 |
| DDM | −8.118 | −0.114 | 0.383 |
| DBSE | −7.366 | −1.580 | 0.696 |

[a] For $Ph_3P$: $E_{HOMO} = -9.270$; $E_{LUMO} = +0.057$.

than that in Figure 2(*a*), which is the pathway involving least nuclear motion,[12] on the assumption that there is complete conjugation of the C–N–N–P centres. There does not appear to be any direct structural evidence for this.† It is noteworthy, however, that in related symmetrical azines RR′C=N–N–CRR′, the angle between the planes of the two RR′C=N– moieties has been suggested,[13] on the basis of dipole moment measurements, to be as high as 70° when R,R′ are alkyl groups, but *X*-ray studies of, for example, PhCH=N–N=CHPh indicate little divergence from total planarity (s-*trans*-conformation).[14] Accordingly, therefore, we prefer to believe that in the present instances the phosphorus centre approaches the diazo-group in the plane defined by the diazo group and the attached *ipso*-carbons of the aromatic rings.

*MNDO Calculations*.—Support for this interpretation of structural effects on the reactivity of the diazo-compounds has been sought by carrying out MNDO calculations of their orbital energies using the MOPAC program package.[15] For 9-diazofluorene structural data are available from *X*-ray crystallography[16] and these were used directly. Such information is not available for the other diazoalkanes and, in particular, the molecular conformation of the $Ar_2C$ portion is not known. The following procedure was, therefore, adopted. *X*-Ray crystallographic data were obtained from the Cambridge Crystallographic Database for the ketones corresponding to the diazoalkanes of interest. These structures were then modified by replacement of the carbonyl oxygen atom by the linear NN grouping using CN and NN bond lengths of 1.321 and 1.127 Å respectively, the values observed directly for 9-diazofluorene. The MNDO calculation was carried out on these structures. Results pertinent to the frontier-orbital argument are given in Table 4.

Before proceeding, however, it is necessary to assess the validity of the calculations.

The calculations refer to the gas phase but are based on structural parameters for the solid phase and are being used in comparison with reactivity in fluid solution. The use of gas-phase calculations in the correlation of reactivity in solution is, we believe, acceptable for acetonitrile as solvent since no specific solute–solvent interactions are present as might have been the case in a protic solvent; instead only dipole–dipole interactions are to be expected, and, while these might diminish differences between one diazoalkane and another, they would not be expected to invert the sequence of energies. We defend the use of crystal geometries as the basis of MNDO calculation on the grounds that intermolecular forces between molecules in the crystal are likely to be subordinate to the more powerful intramolecular forces (steric compression, π conjugation). Moreover, good agreement is obtained between calculation (gas phase) and experiment (*X*-ray crystallography) for the conformation of, for example, benzophenones.[17] We see no way to improve the MNDO calculation in the case of 9-diazofluorene.

The problems arise in the use of bond lengths appropriate to cyclic ketones in calculations on diazoalkanes, particularly in the case of DBSE. Thus the normal polarisation of the ketone carbonyl enhances the aromatic (tropylium) character of the seven-membered ring, whereas this effect is likely to be diminished and even reversed given the electron-rich nature of the diazo-group. Similar effects have been noted in the comparison of bond lengths of the five-membered ring of 9-fluorenone and 9-diazofluorene where the electronic requirements for aromaticity are the reverse of those in DBSE. Although detectable, however, the structural effects of the changed polarisation are fairly small in the fluorene system (<0.02 Å). The effect has been ignored in the present calculations.

The energies of the HOMOs of (**1**)–(**4**) fall in a pattern roughly as expected for orbitals of local $B_1$ symmetry, in which DAF which is best able to accommodate electron density has the lowest energy HOMO and DBSE the highest. Qualitatively the values are reflected in the rates of reaction of the diazoalkanes with acetic acid where a frontier-orbital interaction could be envisaged between the HOMO of the diazoalkane and the LUMO of the transferred proton.

The energies of the LUMOs are surprisingly all negative, especially that for DBSE; this is presumed to be a consequence of the parameterisation. Any errors in individual values are expected to be mitigated by use of energy differences between similar orbitals in different diazoalkanes or HOMO–LUMO separations to correlate reactivities. The ordering of the LUMO energies of (**1**)–(**4**) is quite different from that of the HOMO energies, the values for DDM and DBSA now lying substantially above energies of both DAF and DBSE. The eigenvectors from the MNDO calculation indicate that $E_{LUMO}$ refers to the energy of the lowest orbital of $B_1$ symmetry in each case. By contrast, the energies of the orbitals showing most $\pi^*_{NN}$-character are ordered in a sequence that is the same as that of the HOMOs but with a rather smaller range.

Following the prescription of Huisgen, Sustmann, and co-workers[9] we looked for correlation between $\log k$ for the diazoalkane/$PPh_3$ reaction and $[E_{LUMO}(Ar_2CN_2) - E_{HOMO}(PPh_3)]^{-1} + [E_{LUMO}(PPh_3) - E_{HOMO}(Ar_2CN_2)]^{-1} \equiv F$. The HOMO and LUMO energies for $PPh_3$ were also calculated by MNDO using the geometry derived by *X*-ray crystallography. The values in the footnote to Table 4 were arrived at without inclusion of d orbitals. It should be noted that the simple orbital-energy expression above ignores the numerators in the full FMO treatment which consist of products of orbital coefficients at the reacting centres and the appropriate resonance integrals. Since, for phosphazine formation, one term refers to σ overlap and the other to π, this simplification is more drastic in the present situation than in treating, for example, cycloadditions. A plot of $\log k_2$ *vs.* $F$ is shown in Figure 3, using $E_{HOMO}$- and $E_{LUMO}$-values from Table 4. It can be seen that, while there is an apparent correlation for DAF, DBSA, and DBSE [less good if $E(\pi^*_{NN})$ is used to calculate $F$], this is less than convincing owing to the small number of data points. DDM, however, appears far more reactive than would be expected whether one uses the actual LUMO energy or the energy of $\pi^*_{NN}$. We are led to conclude, therefore, that the simple FMO approach used here is inadequate, perhaps generally so, but particularly for DDM in which there is the possibility that substantial geometrical change in the conjugation within the $Ar_2C$ moiety can occur on passage from reactant to transition state.

Such a conclusion is borne out by the effects of substituents on the reactivity of DDM. Substitution in the *p*-position of both rings by $CH_3O$–, $CH_3$–, or Cl– gives rise to more rapid reaction of the diazoalkane with $PPh_3$ than is observed for DDM itself. This behaviour, which gives rise to U-shaped Hammett plot, is reminiscent of that found in thermal decomposition of the

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† *X*-Ray crystallographic investigations are presently being undertaken.

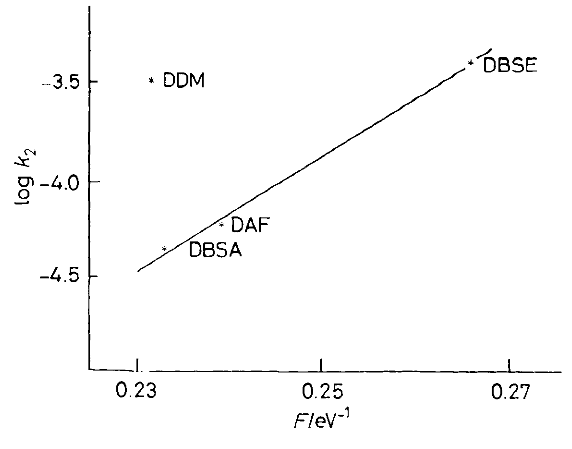

**Figure 3.** Correlation of the reactivity of compounds (**1**)–(**4**) with $F = [E_{\text{LUMO}}(\text{Ar}_2\text{CN}_2) - E_{\text{HOMO}}(\text{PPh}_3)]^{-1} + [E_{\text{LUMO}}(\text{PPh}_3) - E_{\text{HOMO}}(\text{Ar}_2\text{CN}_2)]^{-1}$.

**Table 5.** Phosphazines, $\text{Ar}_2\text{C=NN=PPh}_3$.

| | | | Analysis[a] | | |
|---|---|---|---|---|---|
| Diazoalkane | m.p. | lit. | C | H | N |
| (**1**) | 209–10 | 209–210[b] | | | |
| (**2**) | 168–9 | | 81.8(82.5) | 5.6(5.2) | 5.8(5.8) |
| (**3**) | 177–9 | | 82.1(82.1) | 5.6(5.6) | 5.8(5.8) |
| (**4a**) | 175 | 175[c] | | | |
| (**4b**) | 135–6 | | 70.9(70.9) | 4.5(4.4) | 5.3(5.3) |
| (**4c**) | 164–6 | | 81.9(81.7) | 6.3(6.0) | 5.9(5.8) |
| (**4d**) | 148–50 | | 76.9(76.7) | 5.5(5.7) | 5.4(5.4) |

[a] Figures in parentheses are calculated values. [b] Reference 21. [c] Reference 22.

diazo-compounds[18] and contrasts with the acid-catalysed decomposition of the same compounds.[19] Significantly, the reactivity of substituted triphenylphosphines with DAF gives rise to a linear Hammett plot of negative ρ.[8]

The interpretation of non-Hammett behaviour is often in terms of a change of reaction mechanism but that scarcely seems possible in the present simple reaction. Nor does the simple FMO theory above seem appropriate; DDM already appears to react anomalously quickly and substituents enhance this. It could be argued that the effect of substituents is to increase $F$ by reducing the HOMO–LUMO energy separations but this in itself does not help to explain the rapidity of the reactions. Instead we tentatively suggest that, in passing from reactant DDM to the transition state, a change in conjugation occurs which promotes the reaction. This plausibly could involve rotation of one of the phenyl groups about the bond connecting it to the diazo-carbon atom. With the two aryl rings at right angles, maximum through-conjugation of one with the $\text{C=N}_2$ group is possible, while the π-system of the other can homoconjugate with $\pi_{\text{NN}}$ and $\pi^*_{\text{NN}}$. As the substituent in the 4-position of each ring is varied, the conformation adopted in the transition state is that which most facilitates reaction. In view of the failure of the HOMO–LUMO energy separation from MNDO calculation to predict correctly the relative reactivity of DDM compared with the other three systems, it would seem that, in the transition state, the conformational situation and, therefore, the π conjugation is different from that present in the approximate geometry derived from benzophenone. This apparently simply chemical process should be amenable to more elaborate calculational investigation.

## Conclusions

We have shown that there is an unexpected pattern of reactivity in the reaction of compounds (**1**)–(**4**) with $\text{PPh}_3$ suggesting dominant interaction at the transition state between the diazoalkane as a net electron donor and $\text{PPh}_3$ as a net electron acceptor. An interpretation within FMO theory is qualitatively possible but is not well supported by more quantitative analysis in terms of the HOMO and LUMO energies of the diazo-compounds, at least at the MNDO level. In particular, for DDM, where conformational change affecting orbital energies can occur, the reactivity is higher than expected from frontier orbital energies, and this would seem to be a general weakness of the FMO approach.

## Experimental

*Materials.*—Acetonitrile (Fluka, puriss p.a. or Fison's h.p.l.c. grade) was fractionally distilled from calcium hydride and stored over molecular sieves.

Triphenylphosphine was recrystallised from ethanol, m.p. 80–82 °C, and the diazoalkanes were prepared by oxidation of the corresponding hydrazones (DAF and DDM) or by decomposition of the toluene-*p*-sulphonylhydrazones with potassium methoxide (DBSA and DBSE) as previously described.[18,19,20]

*Phosphazines.*—These were prepared in acetonitrile solution from equimolar amounts of the diazoalkane and triphenylphosphine. When the colour of the diazoalkane was totally discharged the solvent was removed and the residue recrystallised. The products are detailed in Table 5.

*Kinetic Experiments.*—These were carried out in an acetonitrile solution of the diazoalkane (usually *ca.* $10^{-4}$ mol dm$^{-3}$) and triphenylphosphine in large excess so that pseudo-first-order behaviour resulted. For the most part, the reactions were followed spectrophotometrically using a Perkin-Elmer Lambda 5 instrument equipped with a jacketted cuvette holder through which circulated water from a thermostatically controlled bath. Rate coefficients were evaluated from the absorbance of the reaction solution measured at a fixed wavelength, usually in the range 350–400 nm, corresponding to the long wavelength maximum of the phosphazine.

*Calculations.*—Molecular geometries were constructed, examined and manipulated using the CHEM-X (1988) system and calculations were carried out using the MOPAC package within CHEM-X. The energies in Table 4 were the results of a single SCF calculation on each diazoalkane using the geometry defined by the $X$-ray structure of the diazoalkane (DAF)[16] or the ketone related to DBSA,[23] DBSE,[24] and DDM,[25] $X$-ray data for triphenylphosphine are those of Daly.[26]

## Acknowledgements

Financial support from SERC (A. R. N.) and the Iranian Government (M. M. K.) is gratefully acknowledged. The authors appreciated the pungent comments of Dr. D. L. Cooper.

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*Received* 20th *May* 1989; *Paper* 9/02118C