Trico-ordinate Phosphorus Compounds as Catalysts for the Isomerization of (*Z*)- to (*E*)-Azobenzene

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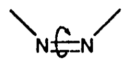
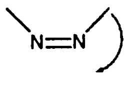
The isomerization of (*Z*)-azobenzene to (*E*)-azobenzene is catalysed by trico-ordinate phosphorus compounds, $Ar_nP(OR)_{3-n}$ where n = 0–2. The reaction is overall second order and for n = 1 and 2, the ρ values of −0.55 and −0.45, respectively, indicate a low degree of charge separation in the transition state. Solvent effects confirm this conclusion and relative rates for n = 0–3 suggest that the transition state is a hybrid of biphilic and polar components.

The phenomenon of *Z–E* isomerism is exemplified by alkenes and azo compounds in which the π-component of the respective carbon–carbon or nitrogen–nitrogen double bonds is resistant to rotation. Hence *Z* and *E* compounds are normally well-defined geometrical isomers which can be interconverted by weakening of the double bond either by heat or light.

A number of theoretical papers[1,2] have discussed the interconversion of *Z* and *E* isomers of azobenzenes and concluded that isomerization occurs either by rotation about the central N=N bond, the rotation mechanism **Ia** or by the planar variation of one of the C–N–N angles, the inversion mechanism **Ib**.

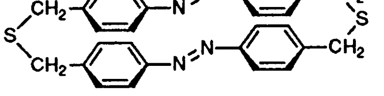


Ia



Ib

Experimental evidence has been provided for both mechanisms in the thermal, *Z–E* isomerization of azo compounds.[3–7] In a later publication, Rau and Luddecke[8] provided unequivocal proof that the direct *Z–E* photo-isomerization of azo compounds could proceed *via* the inversion mechanism by synthesizing two azobenzenophanes (**2** and **3**) in which *Z–E* isomerization by the rotation mechanism was blocked and then observing the *Z–E* isomerization of both spectroscopically. The authors went on to suggest that normal azobenzenes isomerize by a combination of both the rotational and inversional mechanisms.



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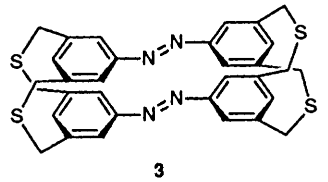

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Studies of the interaction of the phosphorus atom and nitrogen–nitrogen double bonds have been mainly concerned with the reactions of alkyl or arylphosphines with diethyl azodicarboxylate, used widely in the synthesis of sugars[9a] and nucleosides[9b] and pentaco-ordinate phosphorus compounds[10,11] (the Mitsonubo reaction). It was decided, therefore, that a kinetic study of the reactions of a variety of trico-ordinate phosphorus compounds with (*Z*)-azobenzene to afford the *E*-isomer would provide some useful mechanistic information about the attack of the phosphorus atom at the nitrogen–nitrogen double bond.

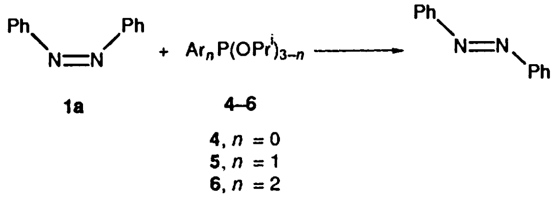
Table 1 Second-order rate coefficients for the phosphinite-catalysed isomerization of *Z*-azobenzene in toluene at 38 °C[a]

$(XC_6H_4)_2POPr^i$	$k_2/10^4$ dm^3 mol^{-1} s^{-1}	σ
X = *p*-Et_2N, H	12.6	−0.90
X = 2 × *p*-MeO	12.2	−0.54
X = *p*-Pr^iO, H	8.32	−0.37
X = *p*-MeO, H	6.55	−0.27
X = 2 × *m*-Me	5.08	−0.14
X = 2 × *p*-MeS	6.92	−0.047
X = 2 × H	5.75	0
X = 2 × *p*-CF_3	1.78	1.08

[a] Linear regression gives: $\log k_2 = -0.45\sigma - 3.25$ (r = 0.97).

Results and Discussion

(*Z*)-Azobenzene was prepared by irradiation (Hg lamp) of the *E*-isomer and isolated by chromatography on neutral alumina.[12] The reaction of **1a** with phosphites **4**, aryl phosphonites **5** or aryl phosphinites **6** were followed by observing the disappearance of the *Z*-azo chromophore at 440 nm. The experimental and kinetic results obtained were as follows.



(*a*) The rate of reaction was found to be overall second order, *i.e.* first order in trico-ordinated phosphorus and the *Z*-azobenzene (Table 4).

(*b*) Using a variety of substituted phosphinites, a ρ value of −0.45 was calculated for toluene as solvent. Table 1 reports the second-order rate coefficient for each phosphinite and Fig. 1 shows the Hammett plot of log k_2 *vs.* σ the substituent constant derived from the ionization of arylcarboxylic acids in water.

(*c*) Similarly, a ρ value of −0.55 (Fig. 2) was obtained using aryl-substituted phosphonites and Table 2 gives the relevant rate coefficients.

(*d*) The relative rates (**6**; X = H):(**5**; X = H):**4** in toluene at 38 °C were 55:7:1. The rate with triphenylphosphine was not

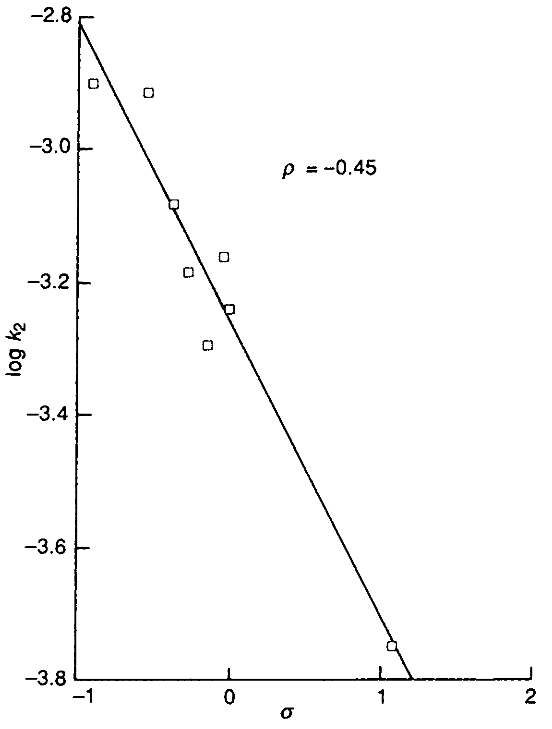


Fig. 1 Plot of log k_2 *vs.* σ for reaction of phosphinites, Ar_2POPr^i, with (*Z*)-azobenzene.

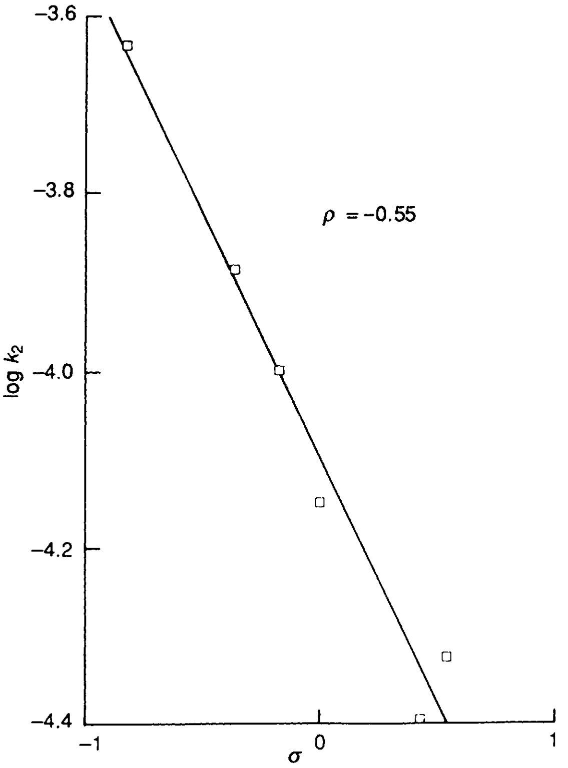


Fig. 2 Plot of log k_2 *vs.* σ for reaction of phosphinites, $ArP(OPr^i)_2$, (*Z*)-azobenzene.

significantly different from the spontaneous (uncatalysed) rate of isomerization.

(*e*) A solvent sensitivity study was carried out on the system using the phosphinite $(p\text{-}Pr^iOC_6H_4)PhPOPr^i$ as catalyst and the results using ethanol, dichloromethane, toluene and acetonitrile are reported in Table 3.

(*f*) No intermediate phosphorus species was detected by ^{31}P NMR spectroscopy during the reactions of **4**–**6** with (*Z*)-azobenzene and there was no detectable reaction between the trico-ordinate phosphorus compounds and (*E*)-azobenzene over a period of ten days at ambient temperature.

Table 2 Second-order rate coefficients for the phosphonite-catalysed isomerization of (*Z*)-azobenzene in toluene at 38 °C[a]

$XC_6H_4P(OPr^i)_2$	$k_2/10^{-5}$ dm^3 mol^{-1} s^{-1}	σ
X = *p*-Me_2N	23.3	−0.83
X = *p*-Pr^iO[b]	13.0	−0.37
X = *p*-Me	10.0	−0.17
X = H	7.09	0
X = *m*-CF_3	3.99	0.43
X = *p*-CF_3	4.74	0.54

[a] Linear regression gives: log $k_2 = -0.55\sigma - 4.10$ ($r = 0.99$). [b] For $(Pr^iO)_3P$ + (*Z*)-azobenzene in toluene at 38 °C, $k_2 = 1.04 \times 10^{-5}$ dm^3 mol^{-1} s^{-1}.

Table 3 Second-order rate coefficients for the *p*-$Pr^iOC_6H_4PhPOPr^i$-catalysed isomerization of (*Z*)-azobenzene in various solvents at 38 °C

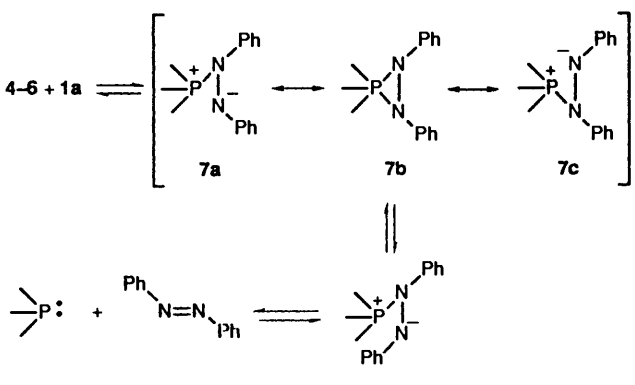
Solvent	$k_2/10^{-4}$ dm^3 mol^{-1} s^{-1}
$C_6H_5CH_3$	8.32
CH_2Cl_2	11.7
CH_3CN	17.2
EtOH	35.7

The kinetic results for the (*Z*)-azobenzene showed a remarkable similarity to those reported for trico-ordinated phosphorus compounds attacking the O–O linkage of peroxides.[13–15] Both systems display low solvent effects and low Hammett ρ values.[13,15] In fact, Lloyd obtained ρ values of −0.2, −0.4 and −0.4 for the reaction of diethyl peroxide with phosphonites, phosphinites and phosphines, respectively, in agreement with Baumstark's value of −0.27 (best correlation with σ^+) for cleavage of the peroxide bond in tetramethyldioxetane.[16] The low ρ values obtained for the (*Z*)-azobenzene system suggest little charge development in the transition state (TS) and this conclusion is entirely consistent with a low sensitivity of the reaction to solvent polarity (Table 3). The reactivity sequence towards (*Z*)-azobenzene is also analogous to the sequence observed with diethyl peroxide as substrate.[13,15] These reactivity trends contrast with sequences obtained for the Michaelis–Arbusov reaction by both Aksnes[17] and Edwards[18] who found $Ph_3P > Ph_2POR > Ph\ P(OR)_2 > P(OR)_3$ for the reactions with ethyl iodide and methyl iodide, respectively. Hence, if one views the latter trend as representing typical nucleophilic (S_N2) displacement reactions by trico-ordinate phosphorus, the (*Z*)-azobenzene and peroxide reactions must occur by a different mechanistic route.

For the peroxide system the anomalous reactivity sequence and low degree of ionic character in the TS have been explained[13–16] by proposing a biphilic mechanism in which the phosphorus displays both nucleophilic and electrophilic character in forming the TS. An analogous mechanism can be invoked to explain the kinetic results for the (*Z*)-azobenzene system. Thus, one can postulate the existence of a high energy intermediate **7** with both ionic and pentacovalent character, *i.e.* a resonance hybrid of three canonical forms **7a**–**c** with **7b** as a major contributor. Rotation about the N–N bond would lead to **8** and hence to (*E*)-azobenzene.

Such a rationalization explains the relative sequence since, for the phosphinites, the trigonal bipyramidal structure of **7b** would require the three-membered ring to have the N atoms apical and equatorial to minimise ring strain which would place two phenyl groups equatorial (lower energy) and one alkoxy group apical (lower energy) as in **9**.

Three-membered ring phosphoranes, although unstable, are



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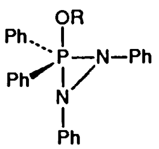

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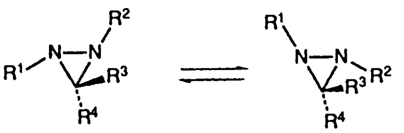

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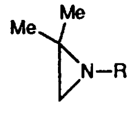

R = Ph, $\Delta G^{\ddagger}$ = 11.2 kcal mol^{-1}

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known to exist as intermediates.[19] Furthermore, even in relatively polar transition states, as in the reaction of trico-ordinated phosphorus with S_8[20] and the desulphurisation of trisulphides[21] there is evidence (anomalous reactivity sequence) to suggest that the TS may have some pentaco-ordinate character.

Assuming the isomerization of the (*Z*)-azobenzene compound occurs after the formation of **7**, both the rotation and/or the inversion mechanisms could be operative in the open chain forms (**7a** and **7c**). Within the pentaco-ordinated form **7b**, however, isomerization could only occur by the inversion mechanism provided the energy barrier for the process was small. Reports in the literature[22,23] reveal that inversion barriers for diaziridine molecules **10** (R = alkyl or benzyl) are sufficiently great to enable the separation of the respective isomeric forms at room temperatures and above. Indeed, when $R^1 = R^4 = Me$, $R^2 = R^3 = PhCH_2$ the $\Delta G^{\ddagger}$ barrier to inversion is 27.3 kcal mol^{-1}.

However, much lower barriers to inversion are obtained for *N*-aryl aziridines (**11**)[24] and there are no reports of the successful separation of *N*-aryldiaziridine isomers at ambient temperature. Hence it is probable, assuming the pentaco-ordinate form **7b** predominates in the intermediate, that isomerisation within this molecule would occur by the inversion mechanism.

In conclusion, it is highly likely that the reaction of (*Z*)-azobenzene with acyclic trico-ordinated phosphorus compounds is mainly concerted, with the sign and size of the ρ values obtained indicating the existence of a small polar component in each reaction. At the very least one may state that if isomerization occurs *via* the dipolar intermediate **8** then very little charge is developed in the transition state leading to its formation.

Table 4 Kinetic data for the reaction of $Ph_2P(OPr^i)$ with (*Z*)-azobenzene in toluene at 38 °C[a]

$[Ph_2POPr^i]$	$k_{obs}/10^{-4}\ s^{-1}$	$k_2/10^{-4}\ dm^3\ mol^{-1}\ s^{-1}$ [b]
0.50	2.85	5.7
0.20	1.12	5.6
0.10	0.59	5.9
0.05	0.29	5.8

[a] $[Z\text{-}Ph_2N_2] = 6.7 \times 10^{-4}$ mol dm^{-3}. [b] Average value of $k_2 = (5.75 \pm 0.15) \times 10^{-4}$ dm^3 mol^{-1} s^{-1}.

Experimental

(*Z*)-*Azobenzene*.—(*Z*)-Azobenzene was prepared using the method of Cook.[12] (*E*)-Azobenzene (1 g, 5.5×10^{-3} mol) in light petroleum (b.p. 40–60 °C) was irradiated for 30 min using a Hg vapour lamp. The resulting solution was filtered through an alumina column and the unchanged *E*-isomer washed through with light petroleum (100 cm^3). The *Z*-compound remained adsorbed on the column and was subsequently eluted using light petroleum (150 cm^3) containing 1–2% methanol. The methanol was removed by washing with water and the organic layer was dried over sodium sulphate. Filtration and removal of solvent under reduced pressure gave orange-red crystals (0.1 g, 10%). Recrystallisation from light petroleum gave orange-red plates, m.p. 70–71 °C (lit.,[12] 71 °C).

Trico-ordinate Phosphorus Compounds.—The diaryl phosphinites, aryl phosphonites and triisopropyl phosphite were prepared and purified as described previously.[15]

The Reaction of Isopropyl p-*Isopropoxyphenylphenylphosphinite with* (Z)-*Azobenzene*.—The phosphinite (0.17 g, 5.5×10^{-4} mol) in deuteriated benzene (1 cm^3) was added to a solution of (*Z*)-azobenzene (0.1 g, 5.5×10^{-4} mol) in benzene (1 cm^3) in a ^{31}P NMR tube. ^{31}P NMR spectra were taken every hour for 8 h and no phosphorus species, other than the reactant trico-ordinate, was detected. After 24 h, a final ^{31}P NMR spectrum was taken with revealed one absorption at $\delta = 105.2$ corresponding to the reactant phosphinite.

The Catalytic Isomerization of (Z)- *to* (E)-*Azobenzene by Phosphorus Nucleophiles*.—A stock solution of (*Z*)-azobenzene in dry ($LiAlH_4$) toluene (0.1 mol dm^{-3}) was prepared and a Pye-Unicam 1700 spectrophotometer employed to observe the disappearance of the chromophore at 440 nm, characteristic of the *Z*-isomer.

Pseudo-first-order conditions in trico-ordinate phosphorus were used in which a cuvette containing the phosphorus nucleophile in dry toluene (3 cm^3, 0.5 mol dm^{-3}) was thermostatted at 38 °C and 20 mm^3 of the stock (*Z*)-azobenzene (0.1 mol dm^{-3}) solution injected to give an absorption of 0.5 Å with at least a twentyfold excess of trico-ordinate phosphorus compound over the substrate.

First-order rate coefficients (k_{obs}) were obtained from the gradients of plots of ln $(A_\infty - A_t)$ *versus* time. Second-order rate constants (k_2) were calculated by dividing the k_{obs} values by the initial concentration of the phosphorus nucleophile. An example of the data obtained for isopropyl diphenylphosphinite is shown in Table 4.

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