Reaction of Phosphetan Oxides with Sulphonyl Isocyanates and Related Reactions

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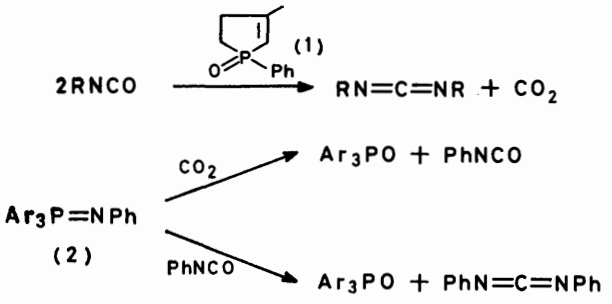
Phosphetan oxides (5) react with toluene-*p*-sulphonyl isocyanate (TsNCO) and chlorosulphuryl isocyanate (CSI) in a variety of solvents to give phosphetan imides [(6) or (7)] with retention of configuration. Phosphetans (8) can be converted into the corresponding imides (6) by using tosyl azide or TsNCO, also with retention of configuration. Alkaline hydrolysis of the imides (6) proceeds with no loss of chirality. The mechanisms of these reactions are discussed.

THE formation of carbodi-imides from isocyanates by the catalytic action of phosphine oxides is well characterised.[1] Campbell and his colleagues have shown that aromatic and aliphatic isocyanates are converted, in high yield, into carbodi-imides under mild conditions with phosphine oxides as catalysts. Moreover the best catalyst was shown to be a compound now known to be the phospholen oxide (1).[2]

[1] J. J. Monagle, T. W. Campbell, and H. F. McShane, *J. Amer. Chem. Soc.*, 1962, **84**, 4288.

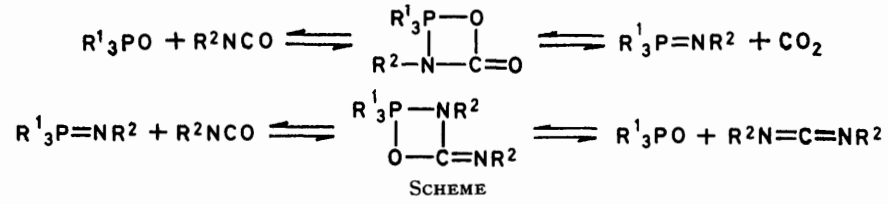
[2] L. D. Quin, J. P. Gratz, and T. P. Barket, *J. Org. Chem.*, 1964, **33**, 1034.

It was demonstrated that phosphine imides (2) prepared by the action of an aromatic azide on tertiary



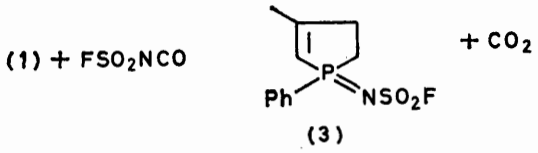
phosphines react with carbon dioxide to give an isocyanate and the corresponding phosphine oxide.[1] The reaction of phosphine imides with isocyanates gave carbodi-imides.

These facts and kinetic evidence led Campbell to propose a mechanism for this reaction which is outlined in the Scheme. The reaction involves slow formation of a phosphine imide by nucleophilic attack of the phosphine oxide oxygen, to form a four-membered ring intermediate or transition state, collapse of which results in elimination of carbon dioxide. The formation of the carbodi-imide is believed to proceed by nucleophilic attack of the nitrogen of the imide on another molecule of isocyanate *via* a similar transition state, which decomposes to carbodi-imide with regeneration of the catalyst.



SCHEME

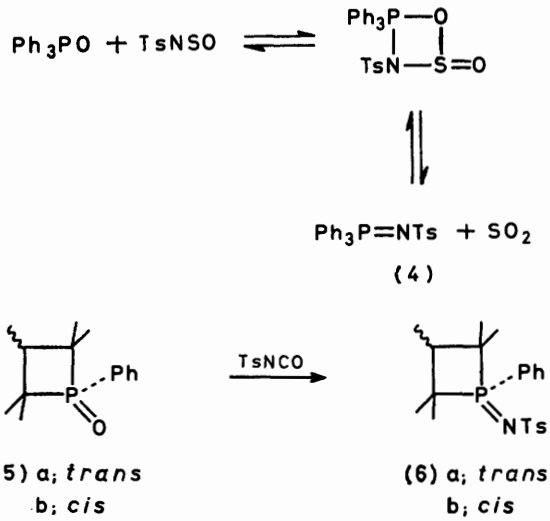
Hoffmann [3] has more recently described the reaction of the phospholen oxide (1) with fluorosulphuryl isocyanate: no carbodi-imide is obtained because the reaction does not proceed beyond the intermediate phospholen *N*-fluorosulphonylimide (3).



In a related reaction, triphenylphosphine and *N*-sulphinyltoluene-*p*-sulphonamide (TsNSO) gave a low yield of triphenylphosphine *N*-(*p*-tolylsulphonyl)imide (4).[4]

Both isomers of 2,2,3,4,4-pentamethyl-1-phenylphosphetan 1-oxide (5) * react with TsNCO remarkably smoothly. Addition of the isocyanate to an ice-cooled solution of a single isomer of the phosphetan oxide in benzene gave a single isomer of the phosphetan imide (6). The same stereochemical result was obtained whether benzene, acetonitrile, dichloromethane, or pyridine was used as solvent, in contrast to the usual solvent effect observed in similar reactions with sulphoxides.[5] In all cases the yield of (6) was essentially quantitative.

Phosphetan imides (7) could also be formed from the reaction of (5) with chlorosulphuryl isocyanate (CSI). These imides are unstable clear oils. However they undoubtedly have the structures (7a and b). Their i.r. spectra show strong SO_2Cl absorptions at 1 325 and 1 165 for (7a) and 1 322 and 1 165 cm^{-1} for (7b). The mass spectra showed the molecular ions and the n.m.r. spectra the expected absorptions (see Experimental section).



These reactions were again stereospecific. The n.m.r. spectra of the crude products showed no indication of the other isomer. Phosphetan oxides are known to be reduced by trichlorosilane and triethylamine with

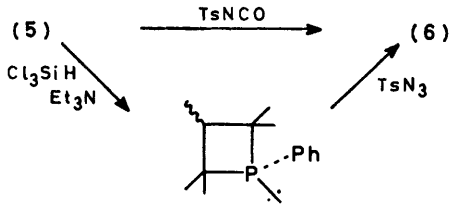
* 1-Phenyl and 3-methyl (a) *trans*, (b) *cis*.

[3] H. Hoffmann, H. Forster, and G. T. Poghossian, *Monatsh.*, 1969, **100**, 311.

[4] A. Senning, *Acta Chem. Scand.*, 1965, **19**, 1755.

[5] F. G. Yamagishi, D. R. Rayner, E. T. Zwicker, and D. J. Cram, *J. Amer. Chem. Soc.*, 1973, **95**, 1916.

retention of configuration at phosphorus.[6] Thus (5) could be reduced to the corresponding phosphetan (8). The reaction of (8) with toluene-*p*-sulphonyl azide in



(8) a; *trans*
b; *cis*

benzene only involves oxidation of the phosphorus lone-pair and it is reasonable to assume therefore that this reaction also proceeds with retention of configuration. Since the *same* phosphetan imide is obtained from both routes and since two of the reactions in the cycle occur with retention of configuration, then the reaction of phosphetan oxides with TsNCO involves retention of configuration at phosphorus.

Phosphetan oxides (5) are, as expected from Campbell's work, very good catalysts for the conversion of *p*-tolyl isocyanate into the corresponding carbodi-imide, but there is no reaction with *N*-sulphinylaniline, TsNSO, or *NN'*-bis-(*p*-tolylsulphonyl)sulphurdi-imide [5] after refluxing in benzene for 2 days.

The kinetics of the reaction of phosphetan oxides with TsNCO were investigated by ^{1}H n.m.r. spectroscopy at −48 °C (Experimental section). The data obtained were substituted into the integrated rate equations for first, second (first in both components), and third order (first in phosphetan oxide, second in TsNCO) rate laws. In each case the reaction was followed to greater than 55% completion. The rate constants were obtained for varying concentrations of tosyl isocyanate, the phosphetan oxide concentration being kept constant (Table).

Rate constants for the reaction of the phosphetan oxide (5a) with TsNCO in $CDCl_3$ at −48 °C

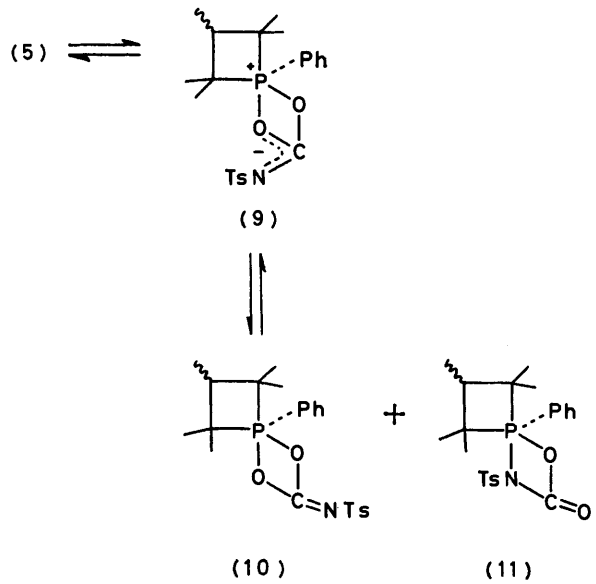
A_0/B_0 [a]	k_2/l mol^{-1} s^{-1} [b]	k_3/l^2 mol^{-2} s^{-1} [b]
1.0	2.4×10^{-4}	5.2×10^{-6}
1.75	3.3×10^{-4}	3.3×10^{-4}
4.9	2.7×10^{-4}	1.8×10^{-3}
1.7	2.9×10^{-4}	

[a] A_0 = initial concentration of TsNCO; B_0 = initial concentration of phosphetan oxide. [b] k_2 and k_3 are second- and third-order rate constants, respectively.

The second-order rate constant does remain constant, whereas the third-order rate constant varies considerably. The predominant reaction can therefore be represented by the rate equation $k_{obs} = k_2$ [phosphetan oxide][TsNCO]. The first step of the reaction of sulphonyl isocyanates with phosphetan oxides is probably nucleophilic attack of the phosphoryl oxygen at isocyanate carbon to give the zwitterion (9). It seems reasonable that this should be the slow step, to be followed by rapid ring closure to (10) or (11) with relief of ring strain and concomitant fragmentation to products.

It is only reasonable to consider ring closure by apical attack of the nucleophile, since equatorial attack would involve the formation of a phosphorane containing a diequatorial four-membered ring. This is known to be a high energy process.[7] Apical attack of the nucleophile opposite one of the ring ligands to give (10) or (11) will entail the relief of ring strain within the phosphetan ring.

Pseudorotation, which would give epimerisation or inversion of stereochemistry at phosphorus, is unlikely since this would again involve an intermediate phosphorane in which one of the four-membered rings was diequatorial. Collapse of (10) regenerates TsNCO and phosphetan oxide with retention of configuration, whereas collapse of (11) leads to (6), with retention of configuration, and carbon dioxide.



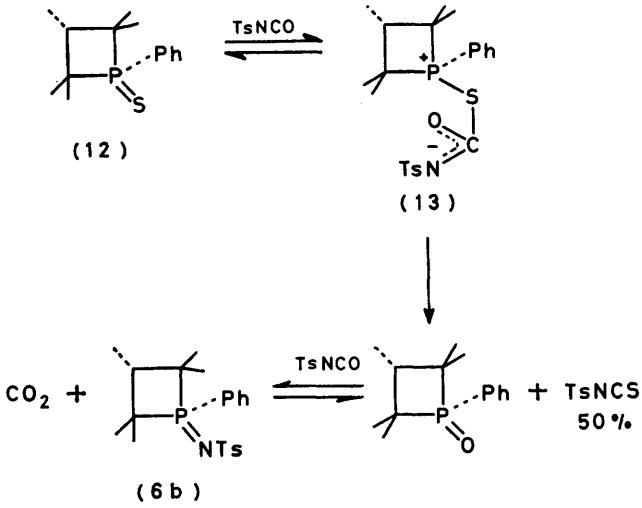
In order to demonstrate that the reaction of the phosphine oxide (5) with TsNCO involves oxygen exchange with retention of configuration, the reaction of the corresponding *cis*-sulphide (12) with TsNCO was investigated. The reaction is much slower than that of the phosphetan oxide under comparable conditions. Addition of 1 mol. equiv. of TsNCO to a solution of (12) gives a final product which contains 0.5 mol. equiv. of unchanged phosphetan sulphide and 0.5 mol. equiv. of phosphetan imide (6b), with retention of configuration at phosphorus. Half the added tosyl group ends up in the imide and the other half is recovered as toluene-*p*-sulphonyl isothiocyanate (TsNCS). This suggests that the reaction proceeds to give an intermediate phosphetan oxide (5b), which then reacts more rapidly than phosphetan sulphide with a second molecule of TsNCO to give the observed imide (6b). Apparently the reaction

[6] (*a*) R. J. Chorvat and S. E. Cremer, *J. Org. Chem.*, 1967, **32**, 4066; (*b*) K. E. DeBruin, G. Zon, K. Naumann, and K. Mislow, *J. Amer. Chem. Soc.*, 1969, **91**, 7207.

[7] (*a*) D. Z. Denney, D. B. Denney, and D. W. White, *J. Amer. Chem. Soc.*, 1971, **93**, 2066; (*b*) R. K. Oram, Ph.D. Thesis, University of Leicester, 1972.

(if any) of phosphetan oxide with TsNCS proceeds much more slowly.

Ring closure of the initially formed zwitterion (13) on oxygen will lead to phosphetan oxide, with retention of configuration, and TsNCS. The phosphetan oxide will then react rapidly with a second molecule of TsNCO to give phosphetan imide, with retention of configuration,



and carbon dioxide. Since 2 moles of TsNCO are needed to convert each mole of phosphetan sulphide into phosphetan imide, with equimolar quantities the reaction only reaches 50% completion. TsNCS, once formed, does not react further.

By analogy one would expect the reaction of TsNCO with (5) to involve oxygen exchange with retention of configuration as well as formation of phosphetan imide (6).

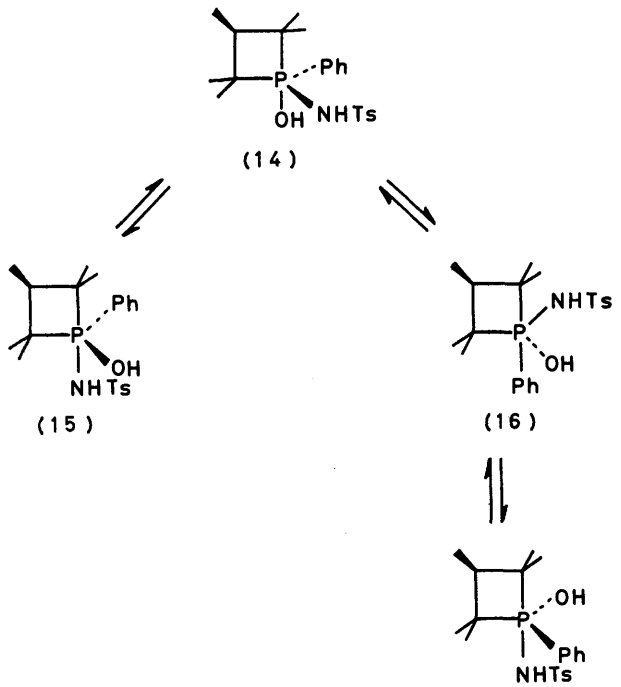
Ring closure of the zwitterion (13) on nitrogen would give the imide (6b) directly and carbonyl sulphide. In order for this process to lead to the observed products the carbonyl sulphide must react immediately and quantitatively with TsNCO to give TsNCS and carbon dioxide.

Alkaline hydrolysis of the single isomers of the imides (6) and (7) in aqueous methanol gave quantitative yields of single isomers of (5). It would be surprising if this hydrolysis had occurred with complete inversion of configuration because of the constraints imposed by the four-membered ring.[8] We infer that these reactions involve retention of configuration at phosphorus, confirming that all the reactions in the cycle, including that of phosphetan oxides (5) with TsNCO, occur with retention of configuration.

The hydrolyses of (6) and (7) can be assumed to involve apical attack of hydroxide ion opposite one of the ring ligands to give an intermediate phosphorane such as (14).[8] If one assumes that pseudorotation processes resulting in a diequatorial phosphetan ring do not occur, then (14) can pseudorotate *via* two pathways to put the leaving group apical. Apical loss of the leaving group from the phosphorane (15) leads to product with retention of configuration, whereas that *via* the phosphorane (16) leads to inversion of configuration. The fact that a quantitative yield of phosphetan oxide with retention of configuration is obtained, in contrast to the lack of stereospecificity in the alkaline hydrolysis of some phosphetanium salts,[9] suggests that pseudorotation of (14) to (16) does not compete with phosphorane decomposition. This can be explained in terms of the observed low apicophilicity of the phenyl group.[10]

The addition of 1 mol. equiv. of CSI to a solution of the *N*-(*p*-tolylsulphonyl)imide (6b) leads to 1 mol. equiv. of *N*-(chlorosulphonyl)imide (7b), with retention of configuration, and 1 mol. equiv. of TsNCO. This reaction reflects the relative nucleophilicities of the phosphetan imide nitrogen atoms and the corresponding electrophilicities of the isocyanate carbon atom.

In contrast to the catalytic conversion of isocyanates into carbodi-imides by phosphine oxides, phosphine *N*-sulphonylimides do not react with sulphonyl isocyanate. This is presumably because the nitrogen of a phosphine *N*-sulphonylimide is much less nucleophilic than that of a phosphine *N*-alkyl- or *N*-aryl-imide. The



phosphorus–nitrogen double bond in both cases is highly polarised, but in phosphine *N*-sulphonylimides the resultant negative charge on nitrogen can be delocalised on to the strongly polar sulphonyl group, thus making the nitrogen less nucleophilic in these cases.

Both TsNCO and CSI react with the phosphetans (8)

[8] See D. J. H. Smith in ' Organophosphorus Chemistry,' Chem. Soc. Specialist Periodical Report, ed. S. Trippett, 1972, vol. 3, p. 20.

[9] J. R. Corfield, M. J. P. Harger, J. R. Shutt, and S. Trippett, *J. Chem. Soc.* (*C*), 1970, 1855.

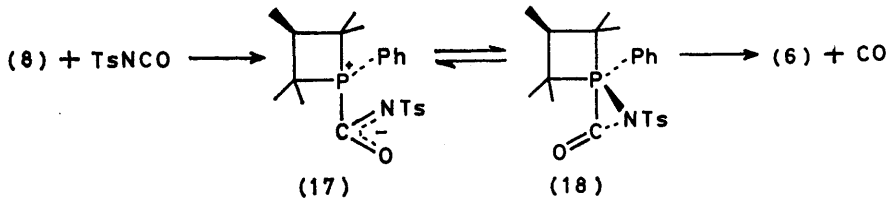
[10] R. K. Oram and S. Trippett, *J.C.S. Perkin I*, 1973, 1300.

in degassed benzene solution to give the respective phosphetan imides (6) with retention of configuration at phosphorus.

Two possible reaction pathways can be considered, *i.e.* for TsNCO either the phosphetan is oxidised by TsNCO to the phosphetan oxide which then reacts with a second molecule of TsNCO to generate the product and carbon dioxide, or there is direct imide formation with loss of carbon monoxide.

Mukaiyama [11] and Hudson [12] have proposed the direct oxidation of cyclic phosphoramidites by phenyl isocyanate. A similar process in this case would generate toluene-*p*-sulphonyl isocyanide which is not observed in the i.r. spectrum of the crude product. Further evidence against an intermediate phosphetan oxide is that the reaction proceeds in yields of up to 85% for equimolar concentrations of starting materials, whereas a process involving 2 moles of TsNCO for each mole of imide formed could not give yields of greater than 50%.

Nucleophilic attack by phosphorus at the isocyanate carbon would give a zwitterion (17). This could undergo



ring closure by nucleophilic attack of the nitrogen at phosphorus to give an intermediate or transition state (18), fragmentation of which would lead to the observed products and carbon monoxide.

Thus all the reactions investigated between phosphetan derivatives and sulphonyl isocyanates proceed with retention of configuration at phosphorus. This is because of the special constraints imposed by the four-membered ring in the phosphorane intermediates. When these constraints are removed, for instance, in acyclic phosphine oxides, the reactions are less stereospecific.[13]

EXPERIMENTAL

I.r. spectra were recorded with a Perkin-Elmer 237 grating spectrometer. Mass spectra were determined with an A.E.I. MS9 instrument. ^{1}H N.m.r. spectra were usually recorded with a Varian T-60 spectrometer (deuteriochloroform as solvent and tetramethylsilane as internal standard unless otherwise stated); 100 MHz spectra were recorded with a JEOL PS100 instrument. ^{31}P N.m.r. spectra were recorded with a JEOL FX-60 instrument. M.p.s were determined with a Kofler hot-stage apparatus.

Solutions in organic solvents were dried over magnesium sulphate and a rotary evaporator was used for reduced pressure solvent removal. All reactions involving air- or moisture-sensitive reactants or products were carried out under dry, oxygen-free nitrogen. Light petroleum had b.p. 40—60 °C.

Small-scale distillations were carried out by using a Kügelrohr; the b.p.s quoted are the oven temperatures at which distillation commenced.

Column chromatography on silica was carried out with Kieselgel 60 PF_{254} (Merck for layer chromatography) with the solvent under a slight positive pressure.

Toluene-*p*-sulphonyl isocyanate (Fluka AG) was fractionally distilled before use. Chlorosulphuryl isocyanate (Aldrich) was distilled from anhydrous potassium carbonate before use.

Reaction of 2,2,t-3,4,4-*Pentamethyl*-r-1-*phenylphosphetan* 1-*Oxide* (5a) *with Toluene*-p-*sulphonyl Isocyanate*.—The isocyanate (0.65 g, 3.2 mmol) was slowly added to an ice-cooled solution of the *trans*-phosphetan oxide [14] (5a) (0.75 g, 3.18 mmol) in benzene (10 ml). A gas was slowly evolved. The reaction was monitored by i.r. spectrometry. The band due to the isocyanate ($\nu_{max.}$ 2 240 cm^{-1}) had disappeared after 30 min. Removal of the solvent under reduced pressure gave 2,2,t-3,4,4-*pentamethyl*-r-1-*phenylphosphetan* N-(p-*tolylsulphonyl*)*imide* (6a) (1.2 g, 97%), m.p. 144 °C (from chloroform–light petroleum), $\nu_{max.}$ (Nujol) 1 265 and 1 150br cm^{-1}, τ 1.75—2.84 (9 H, m), 7.45—8.06 (1 H, m), 7.68 (3 H, s), 8.64 (6 H, d, J_{PH} 19 Hz), 8.81 (6 H, d, J_{PH} 19 Hz), and 9,02 (3 H, dd, J 6 and 1 Hz), *m/e* 389, 374, 325, 215, and 180 (Found: C, 64.8; H, 7.1; N, 3.8. $C_{21}H_{18}NO_2PS$ requires C, 64.8; H, 7.2; N, 3.6%). The reaction was also carried out in acetonitrile, dichloromethane, and chloroform as solvents. Identical products were obtained.

Reaction of 2,2,c-3,4,4-*Pentamethyl*-r-1-*phenylphosphetan* 1-*Oxide with Toluene*-p-*sulphonyl Isocyanate*.—An identical procedure using *cis*-phosphetan oxide [14] (5b) (0.30 g, 1.28 mmol) and toluene-*p*-sulphonyl isocyanate (0.26 g, 1.30 mmol) gave 2,2,c-3,4,4-*pentamethyl*-r-1-*phenylphosphetan* N-(p-*tolylsulphonyl*)*imide* (6b) (1.16 g, 94%), m.p. 179—180° (from chloroform–light petroleum), $\nu_{max.}$ (Nujol) 1 270, 1 140, and 1 100 cm^{-1}, τ 2.24—3.10 (9 H, m), 7.10—7.65 (1 H, m), 7.76 (3 H, s), 8.45 (6 H, d, J_{PH} 19 Hz), 8.75 (6 H, d, J_{PH} 19 Hz), and 9.04 (3 H, dd, J 7.5 and 1 Hz), *m/e* 389, 374, 236, 221, 215, and 180 (Found: C, 64.6; H, 7.05; N, 3.8%).

Hydrolysis of the Imides (6).—A solution of the *trans*-phosphetan imide (6a) (0.18 g, 0.46 mmol) in methanol (10 ml) and aqueous potassium hydroxide (5 ml; 10%) was stirred at room temperature for 2 h, then poured into an excess of water and extracted with dichloromethane. The organic layer was washed with water. Removal of the solvent under reduced pressure gave *trans*-phosphetan oxide (5a) (0.11 g, 98%), m.p. and mixed m.p. 125—126°. An identical procedure with the *cis*-phosphetan imide (6b) gave the *cis*-phosphetan oxide (5b) (98%), m.p. and mixed m.p. 117—118°.

Reaction of the 2,2,3,4,4-*Pentamethyl*-1-*phenylphosphetans*

[11] T. Mukaiyama and Y. Kodaira, *Bull. Chem. Soc. Japan*, 1966, **39**, 1297.

[12] R. Greenhalgh and R. F. Hudson, *Phosphorus*, 1972, **2**, 1.

[13] C. R. Hall, D. J. H. Smith, and P. Watts, following paper.

[14] J. R. Corfield, Ph.D. Thesis, University of Leicester 1971.

(8) *with Toluene*-p-*sulphonyl Azide*.—A solution of toluene-*p*-sulphonyl azide (0.43 g, 2.18 mmol) in degassed benzene (10 ml) was slowly added to an ice-cooled solution of 2,2,*t*-3,4,4-pentamethyl-*r*-1-phenylphosphetan (8a) [6] (0.32 g, 1.46 mmol) in degassed benzene (20 ml). The solution was stirred at room temperature overnight. Removal of the solvent under reduced pressure gave a clear oil (0.6 g). Fractional crystallisation from chloroform–light petroleum gave the *trans*-phosphetan imide (6a) (0.43 g, 75%) and the *trans*-phosphetan oxide (5a) (0.07 g, 20%). An identical procedure with 2,2,*c*-3,4,4-pentamethyl-*r*-1-phenylphosphetan (8b) [6] gave the *cis*-phosphetan imide (6b) (65%).

Reaction of the 2,2,3,4,4-*Pentamethyl*-1-*phenylphosphetans* (8) *with Toluene*-p-*sulphonyl Isocyanate*.—A solution of the isocyanate (0.28 g, 1.41 mmol) in degassed benzene (15 ml) was slowly added to an ice-cooled solution of the *trans*-phosphetan (8a) (0.31 g, 1.41 mmol) in degassed benzene (10 ml). The mixture was stirred at room temperature overnight. Removal of the solvent under reduced pressure gave the *trans*-phosphetan imide (6a) (0.47 g, 85%), m.p. 144° (from chloroform–light petroleum). An identical procedure with the *cis*-phosphetan (8b) gave the *cis*-phosphetan imide (6b) (75%), m.p. 179—180° (from chloroform–light petroleum).

Reaction of the 2,2,3,4,4-*Pentamethyl*-1-*phenylphosphetan* 1-*Oxides* (5) *with Chlorosulphuryl Isocyanate*.—Chlorosulphuryl isocyanate (CSI) (0.21 g, 1.49 mmol) was slowly added to a stirred solution of the *trans*-phosphetan oxide (5a) (0.35 g, 1.49 mmol) in dichloromethane (10 ml) at −40 °C. The solution was allowed to warm to room temperature and the solvent was removed under reduced pressure to give 2,2,t-3,4,4-*pentamethyl*-r-1-*phenylphosphetan* N-(*chlorosulphonyl*)*imide* (7a) (0.49 g, 98%), as an unstable clear oil, $\nu_{max.}$ (CH_2Cl_2) 1 470, 1 325, 1 165br, and 1 005, cm^{-1}, τ 1.64—2.17 (5 H, m), 7.25—7.78 (1 H, m), 8.38 (6 H, d, J_{PH} 19 Hz), 8.68 (6 H, d, J_{PH} 21 Hz), and 8.93 (3 H, dd, J_{PH} 7, J_{HH} 2 Hz), *m/e* 335, 333, 298, 236, 221, 168, 166, 164, 119, and 108. An identical procedure with the *cis*-phosphetan oxide (5b) gave 2,2,c-3,4,4-*pentamethyl*-r-1-*phenylphosphetan* N-(*chlorosulphonyl*)*imide* (7b) (98%) as an unstable, clear oil, $\nu_{max.}$ (CH_2Cl_2) 1 465, 1 322, 1 165br, and 1 000 cm^{-1}, τ 2.00—2.48 (5 H, m), 7.17—7.62 (1 H, m), 8.49 (6 H, d, J_{PH} 18 Hz), 8.69 (6 H, d, J_{PH} 21 Hz), and 9.04 (3 H, dd, J_{PH} 7 Hz, J_{HH} 1 Hz), *m/e* 335, 333, 236, 221, 168, 166, 119, and 108.

Reaction of the 2,2,3,4,4-*Pentamethyl*-1-*phenylphosphetans* (8) *with Chlorosulphuryl Isocyanate*.—Chlorosulphuryl isocyanate (0.28 g, 2.0 mmol) was slowly added to an ice-cooled solution of the *trans*-phosphetan (8a) (0.43 g, 1.95 mmol) in degassed benzene (10 ml). After 10 min the solution was allowed to warm to room temperature and the solvent was removed under reduced pressure. The n.m.r. spectrum of the resulting clear oil showed that no *cis*-product was present. Trituration with ether–light petroleum gave the *trans*-phosphetan imide (7a) (0.34 g, 53%). An identical procedure with the *cis*-phosphetan (8b) gave the *cis*-phosphetan imide (7b) (55%). The n.m.r. spectrum of the crude reaction mixture showed that no *trans*-product was present.

Hydrolysis of the N-(*Chlorosulphonyl*)*imides* (7).—A solution of the *trans*-phosphetan imide (7a) (0.20 g, 0.6 mmol) in methanol (10 ml) and aqueous potassium hydroxide (5 ml; 10%) was stirred at room temperature for 2 h, poured into an excess of water, and extracted with dichloromethane. The combined organic layers were washed with water. Removal of the solvent under reduced pressure gave the *trans*-phosphetan oxide (5a) (0.14 g, 99%). An identical procedure with the *cis*-phosphetan imide (7b) gave the *cis*-phosphetan oxide (5b) (98%).

Reaction of 2,2,c-3,4,4-*Pentamethyl*-r-1-*phenylphosphetan Sulphide* (12) *with Toluene*-p-*sulphonyl Isocyanate*.—The isocyanate (0.074 g, 0.38 mmol) was slowly added to an ice-cooled solution of the *cis*-phosphetan sulphide (12) (0.09 g, 0.38 mmol) in deuteriochloroform (2 ml). The solution was kept at room temperature overnight. The n.m.r. spectrum of the crude product showed the presence of the *cis*-phosphetan sulphide (12) (50%) and the *cis*-phosphetan imide (6a) (50%). The i.r. spectrum of this solution showed strong absorption at 1 900 and none at 2 240 cm^{-1}.

Reaction of the cis-*Phosphetan* N-(p-*Tolylsulphonyl*)*imide* (6b) *with Chlorosulphuryl Isocyanate*.—Chlorosulphuryl isocyanate (0.013 g, 0.096 mmol) was slowly added to an ice-cooled solution of the *cis*-phosphetan *N*-(*p*-tolylsulphonyl)imide (6b) (0.40 g, 0.096 mmol) in deuteriochloroform (1.5 ml). The n.m.r. spectrum of this solution showed the presence of the *cis*-phosphetan *N*-(chlorosulphonyl)-imide (7b) (*ca.* 100%). The i.r. spectrum showed strong absorption at 2 240 and none at 2 250 cm^{-1}.

Reaction of the cis-*Phosphetan Oxide* (5b) *with* p-*Tolyl Isocyanate*.—*p*-Tolyl isocyanate (0.3 g, 2.3 mmol) was slowly added to a solution of the *cis*-phosphetan oxide (5b) (0.1 g, 0.4 mmol) in benzene (10 ml). The solution was set aside overnight. The i.r. spectrum showed strong absorption at 2 130 and none at 2 275 cm^{-1}. The n.m.r. spectrum in deuteriochloroform showed the presence of only the *cis*-phosphetan oxide (5b) and *p*-tolylcarbodi-imide.

Attempted Reactions of the trans-*Phosphetan Oxide* (5a) *with* N-*Sulphinylaniline*, N-*Sulphinyltoluene*-p-*sulphonamide, and* NN′-*Bis*-(p-*tolylsulphonyl*)*sulphurdi-imide*.—*N*-Sulphinylaniline (0.37 g, 2.7 mmol) was slowly added to a solution of the *cis*-phosphetan oxide (5b) (0.60 g, 2.5 mmol) in benzene (5 ml). The solution was refluxed for 2 days. The i.r. and n.m.r. spectra of the mixture showed the presence of only starting materials. Identical results were obtained when dichloromethane or acetonitrile was used as solvent. An identical procedure with *N*-sulphinyltoluene-*p*-sulphonamide or *NN′*-bis-(*p*-tolylsulphonyl)sulphurdi-imide also gave only starting materials.

Kinetic Measurements.—*Reaction of* 2,2,t-3,4,4-*pentamethyl*-r-1-*phenylphosphetan*-1-*oxide* (5a) *with toluene*-p-*sulphonyl isocyanate*. The reactions were run in n.m.r. tubes in the thermostatic probe compartment (−48 ± 1 °C) of a JEOL PS100 spectrometer. The percentage reaction was calculated by comparing the relative intensities of the absorptions due to two equivalent methyl groups in the starting material and the same groups in the product by a cutting and weighing technique. The required amount (1 ml) of a stock solution of the *trans*-phosphetan oxide (0.167M) in ethanol-free deuteriochloroform was allowed to equilibrate in the n.m.r. tube at −48 °C under dry nitrogen. Toluene-*p*-sulphonyl isocyanate was added neat through an injection septum using a previously standardised microsyringe, and the solution was shaken rapidly The reactions were followed to greater than 55% completion.

We thank the S.R.C. for a Research Studentship.

[7/107 *Received*, 24*th January*, 1977]