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SOLVOLYSIS OF HIGHLY REACTIVE PHOSPHORUS-SULPHONIC ANHYDRIDES. STEREOCHEMICAL AND CHEMICAL ARGUMENTS FOR PHOSPHATHIACYLIUM CATION FORMATION

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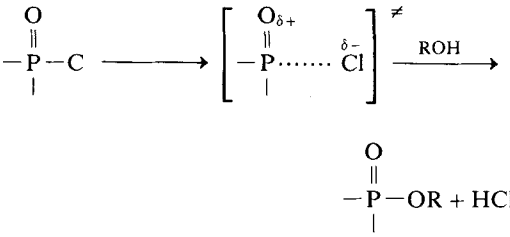
The stereochemistry and mechanism of solvolysis of optically active *tert*-butylphenylphosphinothioic-*O*-trifluoromethanesulphonate (1) in solvents of different ionizing power were studied. It was found that in solvents of high ionizing power and low nucleophilicity 1 ionizes with the formation of a phosphathiacylium cation (2) as the reaction intermediate. Product resulting from the reaction of 2 with anisole was isolated and characterized.

INTRODUCTION

Reactions leading to bond formation or bond breaking around a phosphorus atom belong to the most important processes in biology and biochemistry.[1] Generally, nucleophilic substitution reactions[2] at phosphorus atom follow an associative $S_N2(P)$ mechanism with the formation of a pentacoordinated intermediate (addition–elimination mechanism), or involving a pentacoordinated transition state. A dissociative $S_N1(P)$ mechanism (elimination–addition mechanism) with the formation of a highly reactive metaphosphate intermediate, $ROPO_2^-$, also plays an important role, particularly in reactions of phosphate monoanions, and is well documented.[1b,3] In contrast to the mechanistic pathways mentioned above, the existence of the $S_N1(P)$ mechanism proceeding with the formation of the discrete positively charged tricoordinated species $RR'P^+{=}X$ (X = O, S) has been the subject of both intense study and controversy. Whereas the existence of dicoordinated species of the type $RR'P^+$ is well documented,[4] examples of tricoordinated cations of the type $RR'P^+{=}Y$ (Y = O, S, N, >C−) are rare. Wolf and co-workers[5] reported the synthesis and spectral data of the cations $(R_2N)_2P^+{=}Y$ (Y = S, NR)[5a] and $(R_2N)ClP^+{=}NR'$ (R′ = Ph, P^+Pr^i);[5b,c] however, these cations were not formed in solvolytic processes. The possibility of the participation of phosphacylium-type cations in the reaction course has also been mentioned[6] as a mechanistic option.

A detailed kinetic study of the solvolysis of phosphinic acid chlorides[7] in which the phosphorus atom was surrounded by bulky substituents led to the conclusion that such substrates in highly polar and weakly nucleophilic solvents solvolyse via a dissociative $S_N1(P)$ mechanism [equation (1)].



(1)

Similar conclusions were drawn from kinetic studies of the acid-catalysed solvolysis of phosphinanilides,[8] but other workers[9] opted for an associative *A*2 rather than a dissociative *A*1 mechanism of this reaction. An ionic $S_N1(P)$ mechanism for substitutions at tetracoordinated phosphorus atoms was also rejected on the basis of numerous stereochemical studies.[9c,10] In all instances, inversion of configuration at the phosphorus atom was observed. Partial racemization of the reaction product found in the acid-catalysed solvolysis of phosphinanilides was best explained as a result of nucleophilic catalysis by the conjugate base of the acid catalyst.[9c] More recently, a dissociative character of the acid-catalysed solvolysis of phosphorylimidazoles was proposed.[11] It was found that solvolysis of phosphorylimidazoles was rapid and proceeded with 100% of inversion of configuration. When the starting

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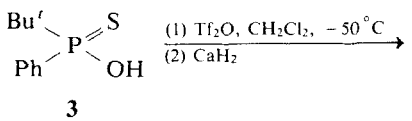
material was treated with tetrafluoroboric acid in non-hydroxylic solvents, a product with retained configuration was also formed. This was attributed to the interaction between an electrophilic intermediate and the solvent. When benzene or anisole was used as the solvent it was claimed that a π-complex with a phosphacylium cation was formed, but no products of electrophilic aromatic substitution were found.

In our earlier studies,[12] ionization of *tert*-butylphenylphosphinothioic-*O*-methanesulphonate under solvolytic conditions was rejected. Nevertheless, the importance of this question to the understanding of solvolytic processes of organophosphorus compounds prompted us to examine the reactivity of highly reactive phosphorus sulphonic anhydrides in which the phosphorus atom is bound to the trifluoromethanesulphonic (triflate) residue, known to be an excellent leaving group.[13] *tert*-Butylphenylphosphinothioic-*O*-trifluoromethanesulphonate (**1**) was chosen as a model compound. It was expected that the presence of a *tert*-butyl group and a triflate group directly bonded to the phosphorus atom would predispose this compound to undergo nucleophilic displacement reactions by a dissociative $S_N1(P)$ mechanism. In this paper, the stereochemical and chemical evidence for the formation of the phosphathiacylium cation **2** from the anhydride **1** under solvolytic conditions is reported.

RESULTS AND DISCUSSION

The synthesis of the anhydride **1** in both racemic and optically active form was achieved[14] by the condensation of *tert*-butylphenylphosphinothioic acid[15] **3** and trifluoromethanesulphonic anhydride in methylene chloride solution at $-50\,^{\circ}C$ [equation (2)].



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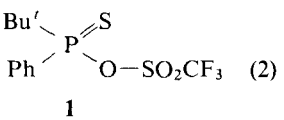
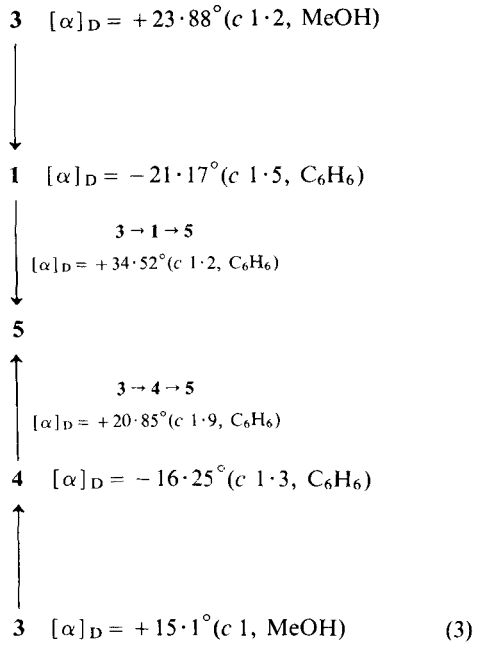


1 (2)

As was expected, the anhydride **1** exhibited a considerably higher solvolytic reactivity under conditions in which previously studied[10a] *tert*-butylphenylphosphinothioic-*O*-methanesulphonate **4** was only moderately reactive. For example, **1** undergoes very fast methanolysis whereas the appropriate reaction of **4** took several days to be completed.

Products resulting from both optically active anhydrides **1** and **4** were formed with high stereoselectivity and with full inversion[10a] of configuration at the phosphorus atom [equation (3)].

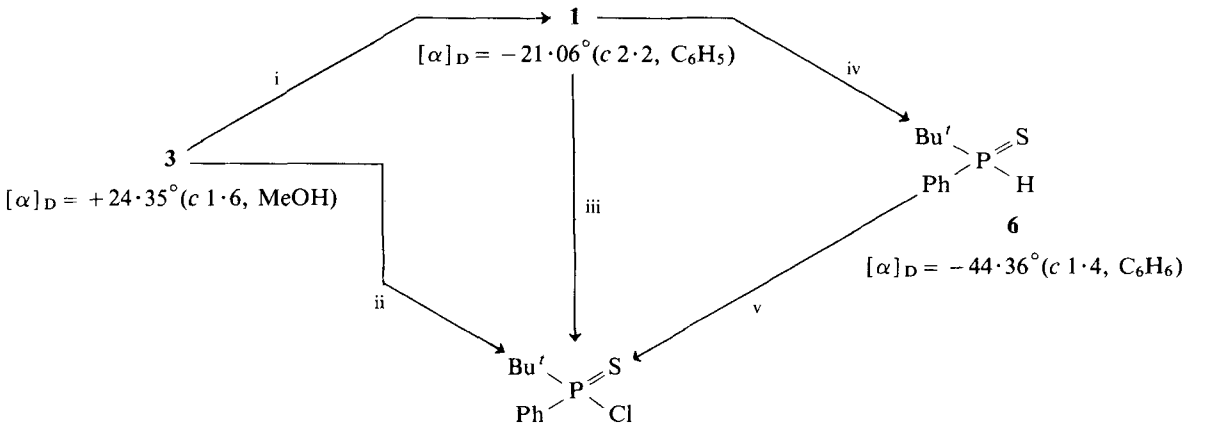


(3)

Inversion at the phosphorus centre and high stereoselectivity were also observed for the reaction of **1** with the chloride anion and with sodium borohydride[14] (Scheme 1).

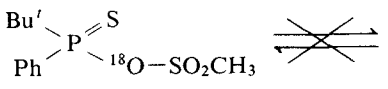
The stereochemistry of the formation of the chloridate **7** and phosphine sulphide **6** from the anhydride **1** can be found from the stereochemical cycle presented in Scheme 1. The formation of **1** (reaction **3** → **1**) occurs without bond breaking around the phosphorus atom. Retention of configuration for this reaction is evident. Also, Todd–Atherton chlorination[16] of the sulphide **6** with carbon tetrachloride in the presence of triethylamine leads to a product with retained configuration. The reaction of the acid **3** with PCl_5 leading to **7** was found[17] to proceed with inversion of configuration. Taking into account that reactions **3** → **1** and **6** → **7** are of known stereochemistry, it can be deduced that the conversions **1** → **7** and **1** → **6** occur with inversion of configuration at the phosphorus atom.

Inversion of configuration is characteristic of the classical $S_N2(P)$ mechanism, but it cannot be excluded that nucleophilic attack occurs as a discrete, rate-determining step involving a contact ion pair formed from **1**. However, such a dissociative pathway was excluded in our previous study[12] on the solvolysis of ^{18}O-labelled anhydride **4** [equation (4)].

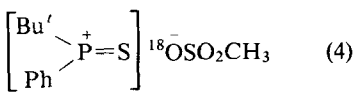


$6 \rightarrow 7$ $[\alpha]_D = -6{\cdot}95°(c\ 1{\cdot}7, C_6H_6)$
$1 \rightarrow 7$ $[\alpha]_D = -6{\cdot}62°(c\ 1{\cdot}5, C_6H_6)$
$3 \rightarrow 7$ $[\alpha]_D = -4{\cdot}80°(c\ 1{\cdot}6, C_6H_6)$

Scheme 1



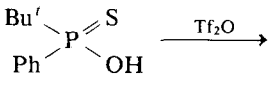
4



8 (4)

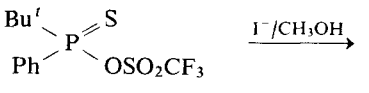
The lack of ^{18}O scrambling which was found in the unreacted substrate was used as an argument against the ionization of **4** leading to the tight ion pair **8**, assuming that the structure of the ion pair which will undergo ^{18}O scrambling is the same as that undergoing solvolysis (ion-pair formation under solvolytic conditions has been discussed in reviews[18]).

The extremely high nucleofugacity of the triflate anion has found extensive use in both synthetic and mechanistic studies.[13] Its ability to depart from esters with the formation of very reactive, even strongly destabilized carbenium ions[13d] implies that also in the solvolysis of **1** the formation of cationic organophosphorus species should be considered. Evidence for ion-pair formation in the solvolysis of **1** came from the inspection of the stereochemistry of the substitution of the triflate group by iodide anion in highly polar solvents. It was found that the reaction of optically active **1** with a methanolic solution of tetrabutylammonium iodide led to the formation of the corresponding ester **5** with inversion of configuration and to the iodidate **9** with retention of configuration [equation (5)].



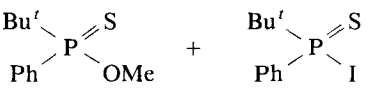
3

$[\alpha]_D = +24{\cdot}35°(c\ 1{\cdot}6, MeOH)$



1

$[\alpha]_D = -21{\cdot}06°(c\ 2{\cdot}2, C_6H_6)$

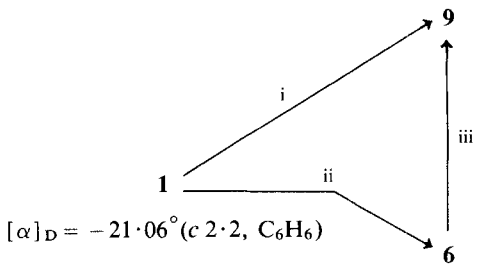


5 **9** (5%)

$[\alpha]_D = +30{\cdot}77°(c\ 1{\cdot}1, C_6H_6)$

$[\alpha]_D = -35{\cdot}66°(c\ 1{\cdot}7, C_6H_6)$ (5)

The stereochemical course of the substitution reaction leading to the iodidate **9** was established on the basis of a stereochemical cycle presented in Scheme 2.



$[\alpha]_D = -21{\cdot}06^\circ$ (c 2·2, C_6H_6)

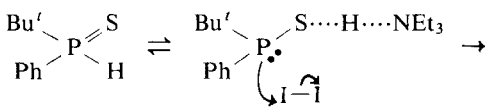
$[\alpha]_D = -44{\cdot}36^\circ$ (c 1·4, C_6H_6)

1 → **9** $[\alpha]_D = -35{\cdot}66^\circ$ (c 1·5, C_6H_6)
6 → **9** $[\alpha]_D = +49{\cdot}79^\circ$ (c 1·9, C_6H_6)

i, $Bu_4N^+I^-$, MeOH
ii, $NaBH_4$, EtOH (−20 °C)
iii, *N*-iodosuccinimide, C_6H_6

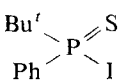
Scheme 2

In a previous study,[14] we found that the chlorination of the optically active phosphine oxide Bu^{t}PhP(O)H by *N*-chlorosuccinimide proceded with retention of configuration. The conversion of the optically active sulphide **6** into the iodidate **9** by *N*-iodosuccinimide[14] probably follows the same reaction mechanism and the same stereochemistry as was observed for *N*-chlorosuccinimide. This assumption is reinforced by the stereochemical result of the reaction of **6** with elemental iodine in the presence of triethylamine [equation (6)].



6

$[\alpha]_D = -42{\cdot}4^\circ$ (c 1·5, C_6H_6)



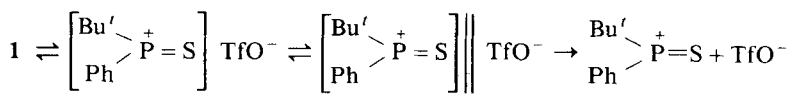
9

$[\alpha]_D = +45{\cdot}6^\circ$ (c 2·4, C_6H_6) (6)

Taking into account that **6** is formed from the anhydride **1** with inversion of configuration (Scheme 1), it is clear that the overall stereochemical result of the formation of **9** via the route **1** → **6** → **9** is also inversion of configuration. Comparison of the signs of the optical rotations of the products **9** obtained via **1** → **6** → **9** and via **1** → **9** indicates that those two products are of opposite configuration. *Retention of configuration observed in the substitution reaction leading to* **9** *was in striking contrast to the generally observed stereochemical course of the $S_N2(P)$ substitution reaction at a phosphorus atom.*[2]

Assuming that the substitution reaction follows an $S_N2(P)$ mechanism, frontal attack of the iodide anion on the phosphorus atom leading to the formation of a pentacoordinated intermediate and its subsequent pseudo-rotation[19,20] should be considered. The second mechanistic option which can account for the stereochemical course of the formation of **9** is the dissociative process with the participation of the cation **2**. According to the Winstein's solvolysis scheme,[18,21] the highly reactive ionic intermediate **2** formed in this reaction should exist in a number of differently solvated ion pairs, each of which can exhibit different reactivity towards nucleophilic reagents (Scheme 3).

Nucleophilic attack on neutral substrate **1** and the tight ion pair **10** should occur with inversion of configuration, whereas attack on free **2** or the solvent-separated ion pair **11** should give racemization or some mixture of inversion and retention, depending on the relative efficiencies of frontal collapse and rear-side



10 **11** **2**

Scheme 3

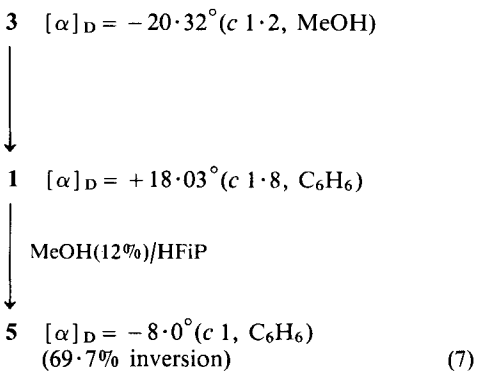
attack. Most probably, steric interactions between the *tert*-butyl group attached to the phosphorus atom and the large iodide anion prevent its rear-side attack on the neutral substrate **1** or the tight ion pair **10**, possibly because this intermediate is far from planar. In consequence, only frontal attack on ion pair **10** is possible.

Important evidence supporting this conclusion was obtained from stereochemical studies performed in solvents of low nucleophilicity and high ionizing power, such as 2,2,2-trifluoroethanol TTFE)[22] and 1,1,1,3,3,3-hexafluoro-2-propanol (HFiP).[23]

In such weakly nucleophilic and highly ionizing solvents, the presence of charged intermediates in the solvolysis reaction should be much more pronounced,[18a,22,23] because of little or no nucleophilic solvent assistance. Indeed, it was found that the solvolysis of optically active anhydride **1** in TFE and HFiP in the presence of tetrabutylammonium iodide gave **9**, but the stereochemistry of the product depended strongly on the ionizing power of the solvent (Scheme 4).

For both TFE and HFiP, the stereoselectivity of the formation of **9** was much lower than was observed when methanol was used as the solvent and, interestingly, the stereochemical pathways of the solvolysis reactions in those two solvents were opposite (a control experiment showed that the low optical purity of the iodidate **9** formed in these reactions is not due to its racemization under reaction conditions).

These results can be rationalized on the basis of the formation of differently solvated ion pairs of **2** (Scheme 3). In methanol, which is highly nucleophilic, the formation of the solvent-separated ion pair **11** or free ion **2** was not likely. The reaction products were formed by the rear-side attack of a small MeOH molecule on **1** or **10** and by nucleophilic attack of the iodide anion on the pair **10** from its less shielded front side. When TFE was used as a reaction medium, the chance for the formation of solvent-separated **11** or the free ion pair **2** increased, which was reflected by the lowering of the stereoselectivity of the formation of **9**. Nevertheless, retention of configuration dominated. In HFiP, ionization of **1** leading to the formation of **11** or even **2** is more likely. As was mentioned above, reaction of the tight ion pair **10** with iodide anion led to the product of retained configuration owing to the steric interactions between attacking nucleophile and groups attached to the phosphorus atom. In **11**, the phosphathiacylium cation **2** probably accepts planar geometry and can be more easily attacked by iodide anion. Inversion of configuration observed in the reaction product **9** suggests that phosphorus atom in the ion pair **11** is attacked more preferably from its less shielded (opposite to the triflate anion) side. Reaction of the planar cation **2** with a nucleophile leads to the racemic product. This mechanistic pathway is also responsible for the low optical purity of the ester **5** formed from **1** when HFiP was used as a solvent and MeOH as a nucleophile [equation (7)]. (It was found that ester **5** is configurationally stable under the reaction conditions).



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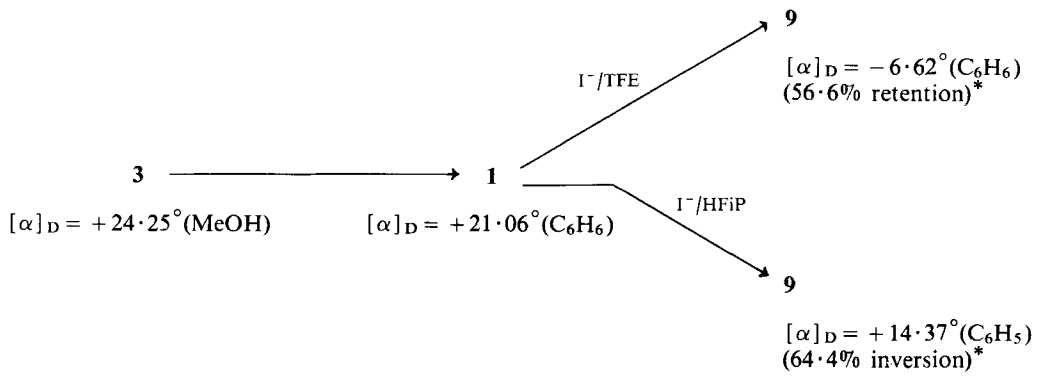
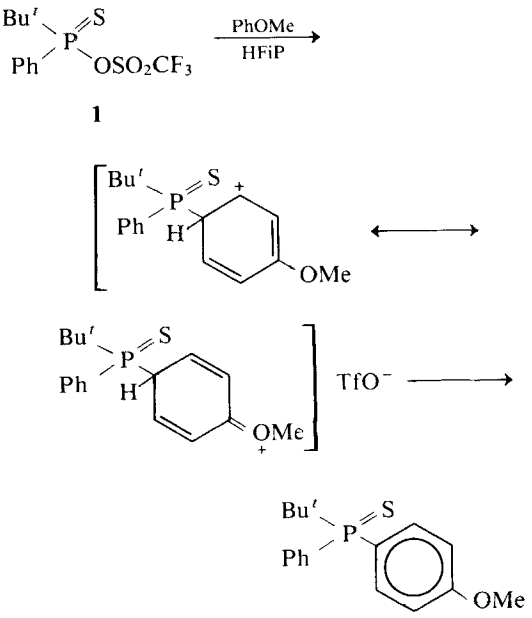


Scheme 4

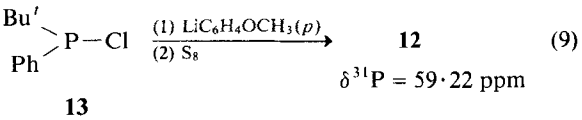
* Calculation is made assuming that the conversion **1** → **6** → **9** (Scheme 2) is stereospecific.

The presence of very reactive ion pairs of **2** in the solvolysis of **1** when HFiP was used as a reaction medium was evidenced by a trapping experiment. It was found that when solvolysis of **1** was performed in HFiP and in the presence of anisole, the product of an electrophilic attack of **2** on the aromatic ring of anisole was formed [equation (8)]. [Product of an electrophilic attack of the cation **2** on the anisole ring was formed in 40% yield (estimated by ^{31}P NMR spectroscopy). Other products resulting from the reaction of **2** with the solvent or from decomposition of **2** were not further analysed]. Sulphide **12** was isolated from the reaction mixture by column chromatography. All spectral ^{1}H NMR, ^{13}C NMR, ^{31}P NMR data and *m/z* values of the isolated compound were in agreement with the structure of **12**. No *ortho* isomer was detected. Probably its formation was inhibited owing to the bulkiness of the groups attached to the phosphorus atom in the cation **2**.



(8)

Additional proof of the structure of **12** was obtained by its independent synthesis from *tert*-butylphenylchlorophosphine (**13**) [equation (9)]. Spectral (^{1}H, ^{13}C, ^{31}P NMR) and chromatographic (GLC, TLC) data for **12** synthesized independently were identical with those of the product of electrophilic attack of **2** on the anisole aromatic ring. *This result represents the first chemical evidence for the existence of phosphathiacylium cation* **2** *formed in a solvolytic reaction* [several attempts were made to observe the formation of the cation **2** by ^{31}P NMR at low temperatures (−70 to 0 °C) in solvents such as HFiP, TFE and nitroethane. No clear data were obtained which could be attributed to the tricoordinated cationic phosphorus species. Also, the stereochemistry of the formation of the phosphine sulphide **12** from the optically active **1**, $[\alpha]_D = -21{\cdot}51°$ (*c* 1, benzene), in HFiP as solvent was investigated. It was found that in this instance reaction product **12** of low optical activity was formed, $[\alpha]_D = -2{\cdot}85°$ (*c* 3, benzene). However, without additional stereochemical study one cannot say what the optical purity and absolute configuration of **12** are]



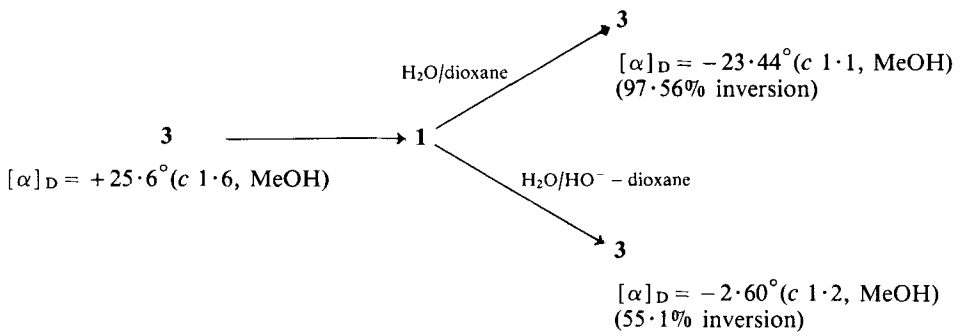
(9)

Stereochemistry of hydrolysis of optically active 1

In a previous study[24] we found that the mechanism of the solvolysis of phosphorus sulphonic anhydrides depended on the pH of the reaction medium. Whereas inversion of configuration was observed at pH < 7, base hydrolysis gave products of retained configuration as a result of $S_N2(S)$ nucleophilic attack of hydroxide ion on the sulphonic sulphur atom or as a result of sulphene formation. Examination of the stereochemical course of the hydrolysis of optically active **1** also revealed a substantial dependence of the optical purity of the reaction product on the pH of the reaction medium (Scheme 5).

For the highly reactive anhydride **1**, which under alkaline conditions cannot react with the formation of a sulphene intermediate, low stereoselectivity of the hydrolysis reaction can be rationalized as a result of frontal attack on the tight ion pair **10** by the bulky, strongly solvated hydroxide ion, or as a result of O—SO_2 and not P—O bond breaking. A clear answer to this question was given by comparison of the results of experiments on the hydrolysis of **1** conducted in ^{18}O-enriched water with the stereochemical course of the hydrolysis of **1** (Scheme 6).

As can be seen, the percentage ^{18}O incorporation into acid **3** resulting in acid or base hydrolysis of **1**, with respect to the ^{18}O enrichment of the reaction medium, is in good agreement with the percentage of inversion which was found for those reactions. It is clear then that retention of configuration at the phosphorus atom causing a loss of the optical purity of the reaction product **3** is due to O—SO_2 bond breaking and that the nucleophilic attack at the thiophosphoryl centre in **1** occurs with full inversion of configuration. This is in accordance with an $S_N2(P)$ mechanism of substitution at the phosphorus atom. The questions of what kind of species is attacked by the molecule of water (tight ion



Scheme 5

pair **10** or neutral molecule of **1**) and what the extents of bond formation and bond breaking in the rate-determining step of the solvolysis reaction of **1** are cannot be answered without detailed kinetic studies.

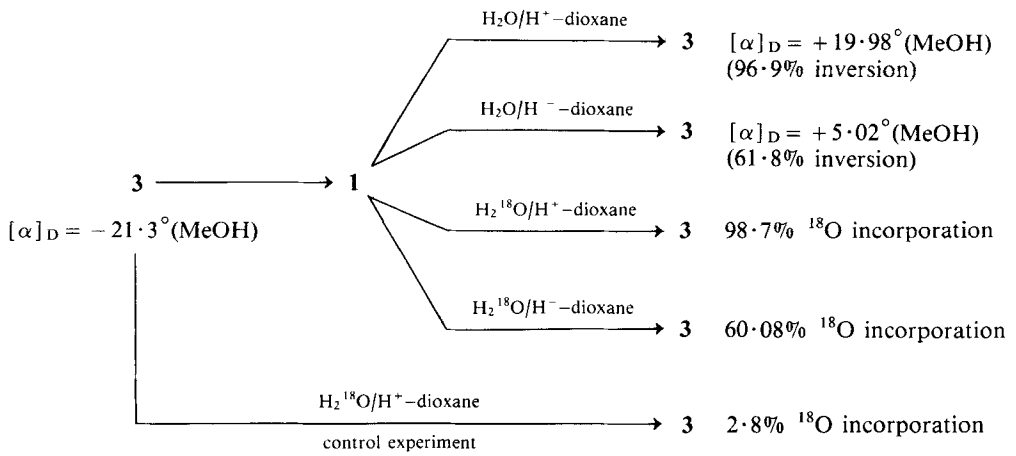
Similarly, inversion of configuration was observed for the reactions of appropriately ^{18}O-labelled phosphate esters[25] for which solvolysis with the formation of a very reactive metaphosphate intermediate was postulated.

Reactivity of 1 in nitromethane

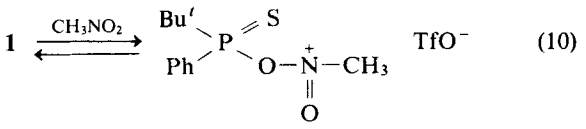
Whereas anhydride **1** is chemically and configurationally stable in dry aprotic solvents of low polarity such as benzene or methylene chloride, it was of interest to investigate its reactivity in an aprotic and highly polar medium.

A stereochemical study of the reactivity of the optically active **1** dissolved in dry nitromethane revealed that **1** is not configurationally stable and undergoes slow racemization. Polarimetric measurements showed that a nitromethane solution of optically active **1** lost about 80 per cent of its initial optical activity after 10 h. Addition of methanol to this solution led to the formation of the ester **5** of low optical purity. The ^{31}P NMR spectrum of the nitromethane solution of **1** revealed that after 12 h the formation of a new product (7 per cent) absorbing at $\delta^{31}P$ 112·6 ppm took place. Addition of MeOH to this sample converted both anhydride **1** and the new product into the methyl ester **5** ($\delta^{31}P$ 107·4 ppm) (CH_3NO_2).

These findings can be explained as the result of the triflate group displacement in **1** by the molecule of nitromethane, leading to the very unstable phosphorus nitronic anhydride **14**, which can be converted back into **1** or can undergo an exchange reaction with another molecule of nitromethane [equation (10)] (an example of a hydrolytically labile phosphorus nitronic anhydride has been reported[26]).

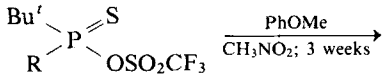


Scheme 6

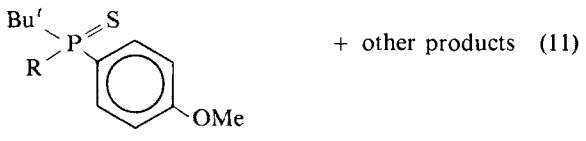


14

Convincing evidence for the dissociative $S_N1(P)$ mechanism of the reaction leading to the racemization of **1** was supplied by the isolation of the phosphine sulphides **12** and **16** [equation (11)].



1 (R = Ph; $\delta^{31}P$ = 129 ppm)
15 (R = Bu^t; $\delta^{31}P$ = 164 ppm)

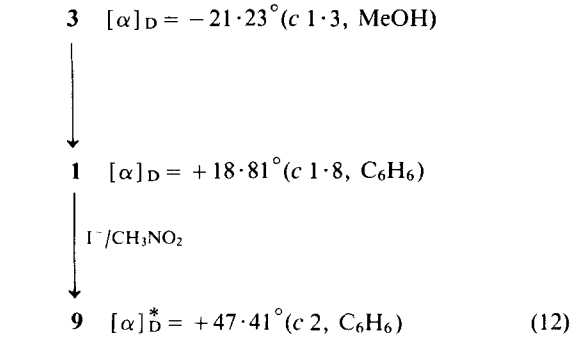


12 (R = Ph; $\delta^{31}P$ = 59·42 ppm)
16 (R = Bu^t; $\delta^{31}P$ = 76·04 ppm)

The sulphide **12** isolated from the reaction mixture was found to be identical (^1H, ^{13}C, ^{31}P NMR and GC–MS data) with the compound synthesized independently [equation (8)]. Also, all spectral data and *m/z* values for the sulphide **16** were in agreement with the proposed structure.

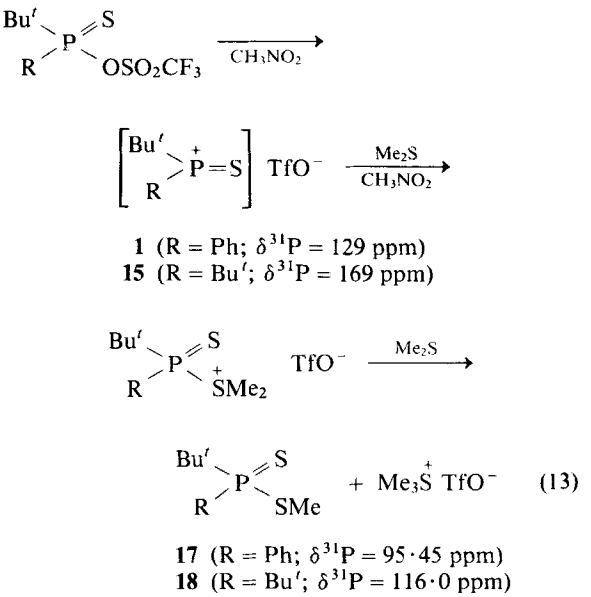
The low yields of **12** and **16** (5 per cent and 4 per cent, respectively) reflect the lower ionizing power of nitromethane compared with HFiP (other components of the complex reaction mixture were not analysed. The complexity of the reaction mixture was due to the instability of the species formed, the long reaction time and the reactivity of nitromethane toward cationic species[27]). Ion pairing in aprotic solvents is important[28] and the amount of highly reactive free cation **2** capable of interacting efficiently with aromatic systems is small. Nevertheless, the formation of **12** and **16** confirms the existence of phosphathiacylium cations formed in a dissociative process from the anhydrides **1** and **15** in nitromethane solution.

The stereochemical course of the substitution reaction of the triflate group in **1** in nitromethane was the same as that observed when methanol was used as a solvent. Also in this instance the retention of configuration found in the reaction of **1** with iodide anion is best explained as the result of the frontal attack of the nucleophile on the tight ion pair **10** [equation (12)].



*(93·7 per cent retention [calculation made assuming that the conversion **1** → **6** → **9** (Scheme 3) is stereospecific].

Most likely, ionization leading to the formation of the phosphathiacylium cation is also responsible for the reaction of the anhydrides **1** and **15** with the neutral molecule of dimethyl sulphide [equation (13)].



1 (R = Ph; $\delta^{31}P$ = 129 ppm)
15 (R = Bu^t; $\delta^{31}P$ = 169 ppm)

17 (R = Ph; $\delta^{31}P$ = 95·45 ppm)
18 (R = Bu^t; $\delta^{31}P$ = 116·0 ppm)

CONCLUSIONS

As already mentioned, several attempts have been made to search for short-lived, positively charged tricoordinate species formed in solvolytic reactions of organophosphorus compounds. The only conclusion that was proposed from those studies was that in the rate-determining step of the reaction extensive bond breaking between the phosphorus atom and the leaving

group take place.[7,8] The observed loss of stereospecificity of the reaction products was rationalized in terms of pseudo-rotation processes,[9c] nucleophilic catalysis[9c] or the influence of extraneous cations.[10c,d] The results presented here provide ample evidence for heterolytic bond cleavage between the phosphorus atom and the triflate group, resulting in the formation of phosphathiacylium cations. Products resulting from the reaction of the phosphathiacylium cation with the aromatic system were detected and isolated. The existence of the cation **2** or ion pairs involving cation **2** is stereochemically manifested only when solvents of high ionizing power and low nucleophilicity (TFE, HFiP) are used or when steric hindrance to the nucleophilic approach to the thiophosphoryl centre plays a critical part.

EXPERIMENTAL

All solvents and commercial reagents were dried and purified by conventional methods before use. NMR spectra were recorded on a Jeol JNM-FX 60 FT or Bruker MSL-300 instrument with 85 per cent orthophosphoric acid as external standard and internal deuterium lock. The Bruker MSL-300 instrument was operated at 121·468 MHz with a quadrature detection system. Products were identified with an LKB Model 2091 gas chromatograph–mass spectrometer. Optical rotations were measured at 589 nm at 20 ± 2 °C on a Perkin-Elmer 141 polarimeter. TLC for monitoring the progress of the reaction was performed on Merck silica gel $60F_{254}$ sheets of 0·25 mm thickness. Column chromatography was performed on Merck silica gel (100–200 mesh). Air- and moisture-sensitive reactions were performed under a blanket of dry nitrogen.

Starting materials. tert-Butylphenylphosphinothioic-*O*-trifluoromethanesulphonate **1** was synthesized as described earlier.[14] Di-*tert*-butylphosphinothioic-*O*-trifluoromethanesulphonate (**15**) was synthesized and purified as described for **1**. Yield 10 per cent; *m/z* 326; ^{31}P NMR ($CDCl_3$), δ 169·1; ^{1}H NMR ($CDCl_3$), δ 1·39 (d, $^3J_{PH}$ 18·12 Hz).

The starting material for the synthesis of **15**, di-*tert*-butylphosphinothioic acid, $Bu^t_2P(S)OH$, was synthesized as follows: to a solution of 7·22 g (0·04 mol) of Bu^t_2PCl[29] in 35 ml of dioxane a solution of 0·725 ml (0·0402 mol) of water and 5·6 ml (0·04 mol) of triethylamine was added and the mixture was stirred for 24 h at room temperature. The resulting precipitate was filtered off and the solvent was evaporated under reduced pressure. The oily residue was dissolved in 10 ml of methanol and 3 ml of 13·5 M KOH and 1·5 g (0·046 mol) of sulphur were added. After stirring for 12 h, excess of sulphur was filtered off. The filtrate was dissolved in 100 ml of water and acidified with concentrated HCl. The product was extracted with CH_2Cl_2 (10 × 15 ml) and the combined extracts were dried over $MgSO_4$ and then evaporated under reduced pressure. The product was crystallized from pentane. Yield 6·8 g (85 per cent); *m/z* 194; ^{31}P NMR ($CDCl_3$, δ 116·9; ^{1}H NMR ($CDCl_3$), δ 1·18 (18H, d, $^3J_{PH}$ 15·92 Hz), 7·2 (1H, s).

tert-Butylphenylphosphinothioic-O-methanesulphonate (**4**). To a solution of 2·14 g (0·01 mol) of acid **3**[14,15] in 100 ml of dry Et_2O a solution of 1·39 ml (0·01 mol) of NEt_3 in 10 ml of dry Et_2O was added. To the resulting solution of the ammonium salt of **3** 1·14 g (0·01 mol) of CH_3SO_2Cl dissolved in 30 ml of Et_2O was added. The reaction mixture was stirred for 12 h at room temperature, then triethylammonium chloride was filtered off and the filtrate was concentrated under reduced pressure. The product was purified by column chromatography (100–200-mesh silica gel, benzene). Yield 1·8 g (60 per cent); ^{31}P NMR (CH_2Cl_2), δ 112·74; ^{1}H NMR (CCl_4), δ 1·21 (9H, d, $^3J_{PH}$ 18 Hz), 3·27 (3H, s), 7·3–8·1 (5H, m). Analysis calculated for $C_{11}H_{17}O_3S_2P$, C 45·2, H 5·82, P 10·6; found, C 45·1, H 5·71, P 10·55 per cent.

Methanolysis of **1** *and* **4**. Reactions were performed by addition of a solution of the corresponding anhydride (0.001 mol) in dry CH_2Cl_2 (0·2–0·5 ml) to methanol (5–10 ml). Progress of the reaction was monitored by TLC. After reaction was completed, the solvent was evaporated under reduced pressure. Ester **5** was isolated by column chromatography on silica gel (100–200 mesh, benzene), R_F = 0·46 (benzene); MS, *m/z* 228; ^{31}P NMR (CH_2Cl_2), δ 107·4; ^{1}H NMR ($CDCl_3$), δ 1·4 (9H, d, $^3J_{PH}$ 13·1 Hz), 3·5 (3H, d, $^3J_{PH}$ 10·9 Hz), 7·3–8 (5H, m).

Reaction of **1** *with chloride anion*. To a solution of 0·150 g (0·00093 mol) of Et_4NCl in 2 ml of dry CH_3CN a solution of 0·270 g (0·00078 mol) of **1** in 0·5 ml of dry CH_2Cl_2 was added. After the reaction was completed, the reaction mixture was concentrated under reduced pressure. The chloridate **7** was purified by column chromatography, R_F = 0·55 (benzene), and was found to be identical (GLC, TLC) with the authentic specimen;[14,17] ^{31}P NMR (CH_2Cl_2), δ 114·69.

Reaction of **1** *with iodide anion leading to* **9**. Reactions were performed by the addition of a solution of **1** (0·0006 mol) to a stiochiometric amount of tetrabutylammonium iodide (TBAI) in 3 ml of the appropriate solvent (CH_3NO_2, TFE or HFiP). For the reaction performed in methanol a 5-fold excess of TBAI was used. After the reactions were completed, excess of solvent was evaporated under reduced pressure. The iodidate **9** was isolated by column chromatography

(100–200-mesh silica gel, benzene), and was found to be identical (GLC, TLC) with the authentic specimen;[14] $R_F = 0{\cdot}54$ (benzene); MS, m/z 324; ^{31}P NMR ($CDCl_3$), δ 83·82; ^1H NMR, δ 1·256 (9H, d, $^3J_{PH}$ 27·57 Hz), 7·4–8·1 (5H, m).

Reaction of **6** *with elemental iodine giving* **9**. To a stirred solution of 0·156 g (0·0008 mol) of the sulphide **6** and 0·080 g (0·0008 mol) of anhydrous triethylamine in 2 ml of benzene–pentane (1 : 1) solution, a solution of 0·2 g (0·00078 mol) of iodine in 2 ml of benzene was slowly added. After addition, the reaction mixture was stirred for 15 min, then washed with 1 ml of saturated $Na_2S_2O_3$ solution. The benzene layer was separated, dried over $MgSO_4$ and concentrated. The iodidate **9** was purified by column chromatography (100–200-mesh silica gel, benzene) and was found to be identical with the authentic specimen.[14]

Solvolysis of **1** *in* HFiP *in the presence of* MeOH *leading to* **5**. To a solution of 0·15 ml of methanol in 1 ml of HFiP a solution of 0·1 g (0·00029 mol) of **1** in 0·1 ml of dry CH_2Cl_2 was added. After the reaction was completed, excess of solvent was evaporated under reduced pressure. The ester **5** isolated by column chromatography (100–200-mesh silica gel, benzene) was identical (GLC, TLC, ^{31}P NMR, MS) with the authentic specimen.

Synthesis of sulphide **12**. To a solution of 0·01 mol of butyllithium in 5 ml of dry Et_2O, a solution of 1·72 g (0·0092 mol) of bromoanisole in 5 ml of Et_2O was added. After stirring for 30 min the reaction mixture was cooled to 0 °C and a solution of 1·84 g (0·00918 mol) of Bu^tPhPCl[15] in 2·5 ml of dry Et_2O was added. After stirring for 1 h at room temperature Et_2O was evaporated under reduced pressure and 5 ml of toluene and 0·4 g (0·0125 mol) of sulphur were added. The reaction mixture was stirred for 2 h at room temperature and excess of sulphur was filtered off. The filtrate was concentrated under reduced pressure. The reaction product **12** was isolated by column chromatography (100–200-mesh silica gel, benzene), $R_F = 0{\cdot}27$ (benzene); yield 2·1 g (75 per cent); MS, $m/z = 304$; ^{31}P NMR ($CDCl_3$), δ 59·22; ^1H NMR ($CDCl_3$), δ 1·235 (9H, d $^3J_{PH}$ 17 Hz), 3·74 (3H, s), 6·89, 7·91 (9H, m); ^{13}C NMR ($CDCl_3$), δ_{PCCH_3} 27·01, δ_{PCCH_3} 36·9, J_{PC} 51·4 Hz, δ_{OCH_3} 56·01, anisole ring $\delta_{C\text{-}(ipso)}$ 122·4, J_{PC} 79·2 Hz, $\delta_{C\text{-}(ortho)}$ 135·62, $^2J_{PC}$ 10·9 Hz, $\delta_{C\text{-}(meta)}$ 114·38, $^3J_{PC}$ 12·4 HZ, $\delta_{C\text{-}(para)}$ 162·6; phenyl ring $\delta_{C\text{-}(ipso)}$ 132·3, J_{PC} 74·4 Hz, $\delta_{C\text{-}(ortho)}$ 133·2, $^2J_{PC}$ 9 Hz, $\delta_{C\text{-}(meta)}$ 128·7, $^3J_{PC}$ 11·3 Hz, $\delta_{C\text{-}(para)}$ 131·7.

Solvolysis of **1** *in HFiP in the presence of anisole leading to* **12**. To a solution of 0·25 ml (0·0023 mol) of anisole in 1·5 ml of HFiP, a solution of 0·23 g (0·00055 mol) of **1** in 0·2 ml of CH_2Cl_2 was added. After 20 min the ^{31}P NMR spectrum of the reaction mixture showed the absence of the starting material. Sulphide **12** was formed with a yield of 40 per cent [^{31}P NMR (HFiP), δ 59·22, 40 per cent]. After concentration of the reaction mixture, **12** was isolated by column chromatography (100–200-mech silica gel, benzene), $R_F = 0{\cdot}27$ (benzene) and was shown to have TLC, GLC MS, ^{31}P NMR, ^1H NMR and ^{13}C NMR data identical with those of the sulphide **12** synthesized independently.

Solvolysis of **15** *in nitromethane in the presence of anisole leading to* **16**. To a solution of 0·04 ml (0·00036 mol) of anisole in 2 ml of dry CH_3NO_2, 0·11 g (0·00033 mol) of **15** was added. The reaction mixture was left at room temperature until no more starting material was present (3 weeks), then concentrated and the sulphide **16** was isolated by column chromatography (100–200-mesh silica gel, benzene), $R_F = 0{\cdot}25$ (benzene), MS, $m/z = 284$; ^{31}P NMR ($CDCl_3$), δ 76·04; ^1H NMR ($CDCl_3$), δ 1·29 (18H, d, $^3J_{PH}$ 15·4 Hz), 3·79 (3H, s), 6·9 (2H, m), 8·05 (2H, m); ^{13}C NMR ($CDCl_3$), δ_{PCCH_3} 24·34, δ_{PCCH_3} 38·49, J_{PC} 43 Hz, δ_{OCH_3} 55·28, aromatic ring $\delta_{C\text{-}(ipso)}$ 120·05, J_{PC} 75 Hz, $\delta_{C\text{-}(ortho)}$ 135·6, $^2J_{PC}$ 9 Hz, $\delta_{C\text{-}(meta)}$ 113·2, $^3J_{PC}$ 11·4 Hz, $\delta_{C\text{-}(para)}$ 161·82.

Solvolysis of **1** *and* **15** *in nitromethane in the presence of dimethyl sulphide* (formation of **17** and **18**). To solution of 0·0002 mol of **1** or **15** in 5 ml of CH_3NO_2, a 4-fold excess of Me_2S was added. Me_2S was refluxed over NaH (30 min) and then distilled from NaH before it was used. After the reaction was completed, excess of solvent was evaporated under reduced pressure. Phosphinodithioates **17** and **18** were isolated by column chromatography (100–200-mesh silica gel, benzene). *S*-Methyl-*tert*-butylphenylphosphinodithioate (**17**):[14] $R_F = 0{\cdot}49$ (benzene); MS, $m/z = 244$; ^{31}P NMR ($CDCl_3$), δ 95·4; ^1H NMR ($CDCl_3$), δ 1·53 (9H, d, $^3J_{PH}$ 18·43 Hz), 2·237 (3H, d, $^3J_{PH}$ 13·11 Hz), 7·3–8·1 (5H m). *S*-Methyl-di-*tert*-butylphosphinodithioate (**18**): $R_F = 0{\cdot}47$ (benzene); MS, $m/z = 224$; ^{31}P NMR ($CDCl_3$), δ 116; ^1H NMR ($CDCl_3$), δ 1·29 (18H, d, $^3J_{PH}$ 26·5 Hz), 2·32 (3H, d, $^3J_{PH}$ 12 Hz).

Alkaline hydrolysis of **1**. A 0·16 g (0·00046 mol) amount of **1** dissolved in 0·5 ml of anhydrous dioxane was added with vigorous stirring to a solution containing 5 ml of dioxane and 5 ml of 0·7 M NaOH. After 5 h the reaction mixture was concentrated to 7 ml and then dissolved in 20 ml of water. Acid **3** was isolated by addition of 1·5 ml of concentrated HCl and then by extraction with $CHCl_3$ (10 × 5 ml). The combined extracts were dried over $MgSO_4$. Acid **3** obtained after evaporation of $CHCl_3$ was dried over P_2O_5. ^{31}P NMR ($CDCl_3$), δ 95·6.

Acid hydrolysis of **4**. A 0·087 g (0·00025 mol) amount of **1** dissolved in 0·3 ml of dry dioxane was added with vigorous stirring to a solution containing 5 ml of dioxane and 5 ml of 0·2 M CF_3SO_3H. The reaction mixture was stirred for 5 h, then concentrated under reduced pressure to 7 ml and dissolved in 20 ml of water. Acid **3** was extracted with $CHCl_3$ (10 × 5 ml) and the combined extracts were dried over $MgSO_4$. Product **3** obtained after evaporation of $CHCl_3$ was dried over P_2O_5. ^{31}P NMR ($CDCl_3$), δ 95·6.

Hydrolysis of **1** *in* ^{18}O*-enriched* H_2O*–dioxane system*. Water with 25·3 per cent ^{18}O enrichment was used. Analysis of ^{18}O enrichment was performed on an LKB Model 2091 gas chromatograph–mass spectrometer combined with a PDP-11/05 computer. Acid **3** was analysed as the *O*-trimethylsilylester, which was introduced through a 10 per cent OV-101 GC column (2·7 m) operated under isothermal conditions (240 °C). Helium was used as the carrier gas (30 ml min^{-1}). Mass sprectra were recorded at an electron energy of 70 eV, trap current 50 μA and ion source temperature 250 °C. Only the molecular peak range $m/z = 260–280$ was scanned. Calculation of ^{18}O enrichment were made using a standard equation[30] based on molecular peaks of m/z 268 and 270.

Alkaline hydrolysis of **1** *in* ^{18}O*-enriched medium*. To a solution of 0·12 g (0·00035 mol) of **1** dissolved in 3 ml of anhydrous dioxane a solution of 3 ml of 0·5 M $Na^{18}OH/H_2{}^{18}O$ (25·3 per cent ^{18}O) was added with vigorous stirring. After stirring for 12 h at room temperature the reaction mixture was concentrated under reduced pressure to 3 ml. Acid **3** was isolated by passing a stream of dry HCl through the solution of its sodium salt and by extraction with $CHCl_3$ (15 × 2 ml). The combined extracts were dried over $MgSO_4$ and then concentrated under reduced pressure. Acid **3** was dried over P_2O_5 (12 h), dissolved in 3 ml of dry Et_2O and treated with Me_3SiCl and NEt_3. Precipitated triethylammonium chloride was filtered off. The ^{18}O enrichment of the reaction product was 15·2 ± 0·2 per cent, which represents 60·08 per cent of the ^{18}O abundance in the reaction medium.

Acid hydrolysis of **1** *in* ^{18}O*-enriched medium*. To a solution of 0·12 g (0·00035 mol) of **1** in 3 ml of anhydrous dioxane a solution of 0·03 ml of CF_3SO_3H in 5 ml of $H_2{}^{18}O$ (25·3 per cent ^{18}O) was added. After stirring for 12 h at room temperature the reaction mixture was concentrated to 3 ml. Acid **3** was extracted with $CHCl_3$ (15 × 2 ml) and converted into the *O*-trimethylsilyl ester as described above. The ^{18}O enrichment of the reaction product was 25·0 per cent ± 0·2 per cent, which represents 98·8 per cent of the ^{18}O abundance in the reaction medium.

Control experiment. To a solution of 0·085 g (0·0004 mol) of acid **3** in 1 ml of anhydrous dioxane, a solution of 0·01 ml CF_3SO_3H in 1 ml of $H_2{}^{18}O$ (25·3 per cent ^{18}O) was added. After 12 h acid **3** was extracted with $CHCl_3$ (15 × 2 ml). The extracts were dried over $MgSO_4$ and then evaporated. The resulting acid **3** was analysed as the *O*-trimethylsilyl ester. The ^{18}O enrichment of the reaction product was 0·73 ± 0·1 per cent, which represents 2·88 per cent of the ^{18}O abundance in the reaction medium.

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REFERENCES

1. (a) D. E. C. Corbridge. *Phosphorous, an Outline of its Chemistry, Biochemistry and Technology*, Ch. 11. Elsevier, Amsterdam (1985); (b) T. C. Bruice and S. J. Benkovic, *Bioorganic Mechanisms*, Vol. 2. Benjamin, New York (1966).
2. (a) R. F. Hudson, *Structure and Mechanism in Organophosphorus Chemistry*. Academic Press, New York (1965); (b) A. J. Kirby and S. G. Warren *Organic Chemistry of Phosphorus*. Elsevier, New York (1967); (c) W. E. McEwan and K. D. Berlin (eds) *Organic phosphorus Stereochemistry, Parts I and II*. Dowden, Hutchinson and Ross, Stroudsburg, PA (1975).
3. F. W. Westheimer, *Chem. Rev.* **81**, 313 (1981).
4. (a) *Methoden der Organischen Chemie (Houben-Weyl), Organische Phosphor-Verbindungen I, E 1*. Geog Thieme Verlag, Stuttgart, New York (1982); (b) E. Fluck in *Topics in Phosphorus Chemistry*, M. Grayson and E. J. Griffith (eds), vol. 10, 193 Wiley, New York (1980); (c) O. Dahl, *Tetrahedron Lett.* **23**, 1493 (1982) (d) A. H. Cowley and R. A. Kemp, *Chem. Rev.* **85**, 367 (1985).
5. (a) M. R. Marre, M. Sanchez and R. Wolf, *Phosphorus Sulfur* **13**, 327 (1982); (b) M. Sanchez and M. R. Marre, J. F. Brazier, J. Bellan and R. Wolf, *Phosphorus Sulfur* **14**, 331, (1983); (c) M. R. Marre, M. Sanchez and R. Wolf *J. Chem. Soc., Chem. Commun.* 566, (1984).
6. (a) J. T. Gupton, J. P. Idoux, G. Baker, C. Colon, A. D. Crews, C. Jurss and R. C. Rampe, *J. Org. Chem.* **48**, 2933 (1983); (b) C. Blonski, M. B. Gasc, A. Klaebe and J. J. Perie, *Tetrahedron Lett.* **23**, 2773 (1982); (c) A. W. Frank, *Phosphorus Sulfur* **5**, 197 (1988); (d) R. Rampe, *J. Chem. Soc., Perkin Trans. 1* 1217 (1985).
7. (a) P. Haake and P. S. Ossip, *J. Am. Chem. Soc.* **93**, 6924 (1971); (b) P. Haake and P. S. Ossip, *Tetrahedron Lett.* **55**, 4841 (1970).
8. (a) D. A. Tyssee, L. P. Bausher and P. Haake, *J. Am. Chem. Soc.* **95**, 8066 (1973); (b) T. Koizumi. Y. Kobayashi and E. Yoshii, *J. Chem. Soc, Chem Commun.* 678 (1974); (c) P. Haake and D. A. Tyssee, *Tetrahedron Lett.* **40**, 3513 (1970).
9. (a) M. J. P. Harger, *J. Chem. Soc., Perkin Trans. 2* 154 (1980; (b) M. J. P. Harger, *J. Chem. Soc., Perkin Trans.*

1 605 (1977); (c) M. J. P. Harger, *J. Chem. Soc., Perkin Trans. 1* 2057 (1977); (d) A. C. Clements, M. J. P. Harger, A. Leonard and M. D. Reed, *Tetrahedron Lett.* **6**, 413 (1976); (e) M. J. P. Harger, A. J. Macpherson and D. Pickering, *Tetrahedron Lett.* **22/23**, 1797 (1975); (f) G. Tomashewski and G. Kühn, *J. Prakt. Chem.* **38**, 222 (1968); (g) T. A. Modro and B. P. Rijkmans, *J. Org. Chem.* **47**, 3208 (1982); (h) T. A. Modro and D. H. Graham, *J. Org. Chem.* **46**, 1923 (1981).

10. (a) B. Krawiecka, J. Michalski and Z. Skryzypczyński, *J. Chem. Soc., Chem. Commun.* 1022 (1974); (b) M. J. P. Harger, *J. Chem. Soc., Chem Commun.* 520 (1976); (c) W. S. Wadsworth, Jr, *J. Org. Chem.*, **38**, 2921 (1973); (d) M. Bauman, W. S. Wadsworth, Jr, *J. Am. Chem. Soc.*, **100**, 6388 (1978); (e) W. S. Wadsworth, Jr, S. Larsen and H. L. Horten, *J. Org. Chem.* **38**, 256 (1972).
11. W. S. Wadsworthg, Jr, *J. Org. Chem.* **52** 1748 (1987).
12. J. Michalski, Cz. Radziejewski, Z. Skrzypczyński and W. Dabkowski, *J. Am. Chem. Soc.* **102**, 7976 (1980).
13. (a) P. J. Stang, M. Hanack and L. R. Subramnian, *Synthesis* 85 (1982); (b) P. J. Stang and M. R. White, *Aldrichim. Acta* **16**, 15 (1983); (c) T. T. Tidwell, *Angew. Chem., Int. Ed. Engl.* **23**, 20 (1984); (d) D. N. Kevill and S. W. Anderson, *J. Org. Chem.* **50**, 3330 (1985) and references cited therein; (e) D. N. Kevill and G. M. L. Lin, *Tetrahedron Lett.* **11**, 949 (1978); (f) X. Creary, *J. Org. Chem.* **50**, 5080 (1985); (g) J. B. Hendrickson, D. D. Sternbach and K. W. Bair, *Acc. Chem. Res.*, **10**, 306 (1977).
14. Z. Skrzypczyński and J. Michalski, *J. Org. Chem.*, **53**, 4549 (1988).
15. H. Hoffman and P. Schnellenbeck, *Chem. Ber.* **99**, 1134 (1966).
16. B. Miller in 'Reactions of TYrivalent Phosphorus Derivatives and Positive Halogen Source', *Top. Phosphorus Chem.* **2**, 133 Wiley Interscience, New York (1965).
17. J. Michalski, M. Mikołajczyk *and J. Omelańczuk, Tetrahedron Lett.* 3565 (1968).
18. (a) T. N. Bentley and P. R. Schleyer, *Adv. Phys. Org. Chem* **14**, 1 (1977); (b) J. M. Harris, *Prog. Phys. Org. Chem.* **11**, 89 (1974); (c) D. J. Harris, J. M. Harris and P. R. Schleyer, in *Ions and Ion pairs in Organic Reactions*, M. Szwarc (ed.), Vol. 2, Wiley, New York (1974).
19. R. Luckenbach, *Dynamic Stereochemistry of Pentacoordinated Phosphorus and Related Elements*, Georg Thieme, Stuttgart (1973).
20. F. W. Westheimer, *Acc. Chem. Rec.* **1**, 70 (1968).
21. (a) S. Winstein, E. Clippinger, A. H. Fainberg and G. C. Robinson, *J. Am. Chem. Soc.* **76**, 2597 (1954); (b) S. Winstein, B. Appel, R. Baker and A. Diaz, *Chem. Soc. Spec. Publ.* No. 19, 109 (1965).
22. T. Ando and S. Tsukamoto, *Tetrahedron Lett.* **32** 2775 (1977).
23. (a) T. N. Bentley and P. R. Schleyer, *J. Am. Chem. Soc.* **98** 7658 (1976); (b) F. L. Schadt, T. N. Bentley and R. P. Schleyer, *J. Am. Chem. Soc.* **89**, 7667 (1976).
24. J. Michalski, Cz. Radziejewski and Z. Skrzypczyński, *J. Chem. Soc. Chem. Commun.* 762 (1976).
25. (a) J. M. Friedman and J. R. Knowles, *J. Am. Chem. Soc.* **107**, 6126 (1985); (b) P. M. Cullis and A. J. Rous, *J. Am. Chem. Soc.* **108**, 1298 (1986); (c) F. Ramirez, J. Marecek, J. Minore, S. Srivastava and W. le Nobel, *J. Am. Chem. Soc.* **108**, 348 (1986); (d) K. W. Y. Abbel and A. J. Kirby. *Tetrahedron Lett.* **27**, 1085 (1968); (e) P. M. Cullis and A. J. Rous, *J. Am. Chem. Soc.* **107**, 6721 (1985); (f) G. Lowe and S. P. Tuck, *J. Am. Chem. Soc.* **108**, 1300 (1986); (g) P. M. Weiss, W. B. Knight and W. C. Cleland, *J. Am. Chem. Soc.* **108**, 2761 (1986); (h) W. B. Knight, P. M. Weiss and W. W. Cleland, *J. Am. Chem. Soc.* **108**, 2759 (1986).
26. R. D. Goreev, G. M. Loginova and A. Pudovik, *Zh. Obsch. Khim.* **46**, 1906 (1976).
27. Y. Pocker, *J. Chem. Soc.*, 240 (1958).
28. D. Bethel and V. Gold *Carbonium Ions* Academic Press, London, New York (1966).
29. M. Field, O. Stelzer and R. Schmutzler, *Inorg. Synth.* **14**, 6 (1973).
30. R. M. Caprioli, in *Biochemical Applications of Mass Spectrometry*, G. Waller (ed.), p 735. Wiley-Interscience, New York (1972).