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STEREOCHEMISTRY OF THE ACYCLIC PHOSPHONO- AND PHOSPHINO-THIOCYANIDE ISOMERISATION INTO CORRESPONDING ISOTHIOCYANIDATES†

SYNTHESIS OF OPTICALLY ACTIVE THIOCYANIDATES >P(O)SCN ISOTHIOCYANIDATES >P(O)NCS, ISOCYANIDATES >P(O)NCO AND RELATED PHOSPHORYLATED DERIVATIVES OF CARBONIC ACID

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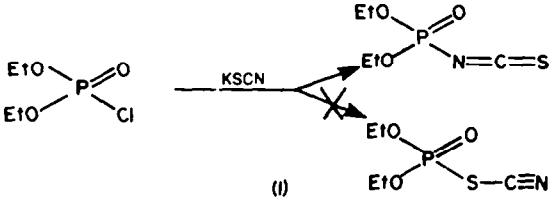
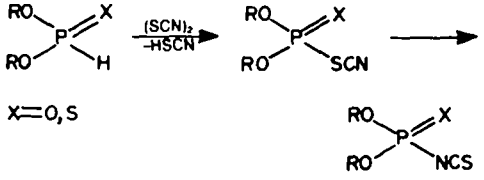
Abstract—Optically active t-butylphenylphosphinothiocyanidate $Bu^tPhP(O)SCN$ **3** and t-butyl-O-methyl-phosphonothiocyanidate $Bu^t(MeO)P(O)SCN$ **7** have been prepared by condensation of the corresponding sulphenyl chlorides >P(O)SCl with trimethylsilylcyanide and isomerised into optically active t-butyl-O-methyl-phosphonoisothiocyanidates $Bu^t(MeO)P(O)NCS$ **8**. Chirality at P in and the optical purity of the chiral phosphino (phosphono) thiocyanidates and isothiocyanidates have been determined by chemical correlations. It has been demonstrated that the thiocyanate ion and amine catalysed *thiocyanidate-isothiocyanidate* isomerisation >P(O)SCN→ >P(O)NCS occurs stereospecifically with inversion of configuration at the P center. This result can be rationalized by postulation of a phosphorane intermediate, formed by nucleophilic attack of the SCN^- anion on phosphorus, in which thiocyanate and isothiocyanate groups occupy apical positions. In connection with these studies a number of novel optically active phosphorylated derivatives of carbonic acid, >P(O)NHCSNHR, $>P(O)NCCl_2$, >P(O)NCO and >P(O)NHCOOBu^t, have also been synthesised.

The formation of phosphoroorganic thiocyanate >P(O)-SCN was first suggested by Saunders *et al.*[3] in the reaction of diethylphosphorochloridate with potassium thiocyanate. It is now well established that this process leads directly to diethylphosphoroisothiocyanidate most likely without intermediacy of the phosphorothiocyanidate.[4,5]



(1)

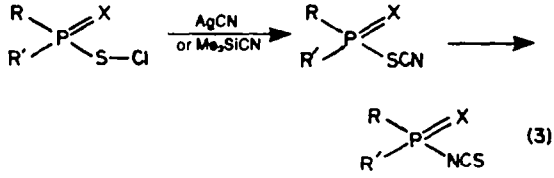
A number of reactions are know however in which the thiocyanidates are likely to be primary products which, subsequently, readily isomerise under the given reaction conditions into more thermodynamically stable isothiocyanidates >P(O)SCN→ >P(O)NCS. The reaction between dialkyl phosphites or thiophosphites and thiocyanogen can be given as an example.[6,7]



(2)

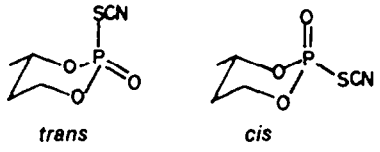
The first "genuine" phosphorothiocyanidate was described by Łopusiński and Michalski in 1972 and its great susceptibility to isomerisation was demonstrated.[8]

The phosphorothiocyanidates were synthesised from oxophosphoranesulphenyl chlorides by displacement reactions at the sulphur centre by silver cyanide[8] or, more conveniently, by trimethylsilyl cyanide.[5,9]



(3)

The stereochemistry of the isomerisation >P(O)SCN → >P(O)NCS was studied by Łopusiński, Michalski and Stec with the aid of a cyclic diastereoisomeric 2-oxo-2-thiocyano-4-methyl-1,3,2-dioxaphosphorianan model system.[5]

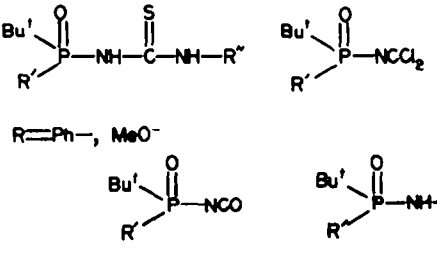


trans *cis*

It has been shown that this rearrangement proceeds with full inversion of configuration at the P atom and is autocatalysed by nucleophilic partners, e.g. SCN^- ion, most likely via a penta-coordinated intermediate of trigonal bipyramid geometry. Other mechanistic pathways including $S_N1(P)$ with transient formation of the phosphacyl cation $(>P{=}O)^+$ are considered unlikely on the basis of the above mentioned results. However, it is feasible that the mechanism of the nucleophilic catalysed *thiocyanidate-isothiocyanidate* isomerisation >P(O)SCN→ >P(O)NCS may depend on the substituent structure at P. It is known that in phosphorus chemistry cyclic systems influence markedly the stereochemical course of displacement reactions at the tetracoordinate P centre.[10] For this reason conclusions based upon cyclic models are subject to some limitations. In order to generalise our previous findings we undertook a study of the *thiocyanidate-isothiocyanidate* isomerisation with optically active t-butyl-phenylphosphinothiocyanidate

†Dedicated to Prof. Leopold Horner on the occasion of his 70th birthday.

Bu^{t}PhP(O)SCN **3** and t-butyl-O-methyl-phosphonothiocyanidate Bu^t(MeO)P(O)SCN **7** as chiral model compounds. They were prepared from t-butylphenylphosphinothioic Bu^{t}PhP(S)OH **1** and t-butyl-O-methylphosphonothioic Bu^t(MeO)P(S)OH **5** acids respectively.[11,12] The advantage of these models is obvious. They are readily available in high optical purity, have pronounced stability and tendency to give crystaline derivatives. The present paper includes also the synthesis of a number of novel optically active phosphorylated carbonic acid derivatives: such as phosphorylated thioureas, isocyaniddichlorides, isocyanates and phosphorylated urethanes.



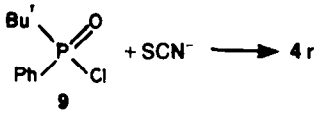
RESULTS

Optically active thiocyanidates **3** *and* **7** *and their isomerisation into isothiocyanidates* **4**, **8**. The primary task of this investigation was to prepare the optically active thiocyanidates **3** and **7** starting from (+)-*R*-**1** and (−)-*S*-**5** thioic acids. The (+)-*R* t-butylphenylphosphinothiocyanidate **3** and (−)-*S*-t-butyl-O-methylphosphonothiocyanidate **7** were synthesized from oxophosphoranesulphenyl chlorides **2** and **6** by replacement of the Cl atom by reaction with trimethylsilyl cyanide. The two chlorides **2** and **6** were obtained by chlorination of the corresponding optically active acids **1** and **5**.

Under mositure free conditions the overall yields are almost quantitative. The ^{31}P NMR and IR spectral data confirm exclusively the thiocyanidate structure of **3** and **7**. The isomerisation of **3** into **4** and **7** into **8** proceeds fast at room temperature in the presence of catalytic amounts of benzyltri-n-butylammonium thiocyanate (0.05%) in benzene solution and is completed within one minute in the case of **3**. The isomerisation of **7** is somewhat slower and requires 30 min for completion. Prolonged reaction times lead to partial racemisation of **4** and **8**. In independent experiments the above mentioned compounds and 0.05% of the tertiary ammonium thiocyanate were allowed to stand in benzene solution at 20°, where upon a slow racemisation occured (**4**, $t_{1/2}^{20} \approx 4 \times 10^5$ sec; **8**, $t_{1/2}^{20} \geqslant 10^6$ sec). The thiocyanidates **3**, **7** and isothiocyanidates **4**, **8** in the absence of nucleophiles such as thiocyanate salts, water and amines are perfectly stable.

It is interesting that the *thiocyanidate-isothiocyanidate* isomerisation proceeds, readily also in the presence of catalytic amounts of pyridine. In this case the stereoselectivity of the rearrangement is slightly lower than that carried out in the presence of benzyltri-n-butylammonium thiocyanate. To gain insight into this point, we examined the stereochemical course of the reaction in relationship to the amounts of pyridine added. The stereoselectivity decreases markedly with increasing amine concentration. Finally the isomerisation in pyridine solution led to almost full racemisation.

The racemic isothiocyanidate **4** can also be readily obtained by nucleophilic displacement of the Cl of the chloridate **9** by the isothiocyano group.[5] By contrast to



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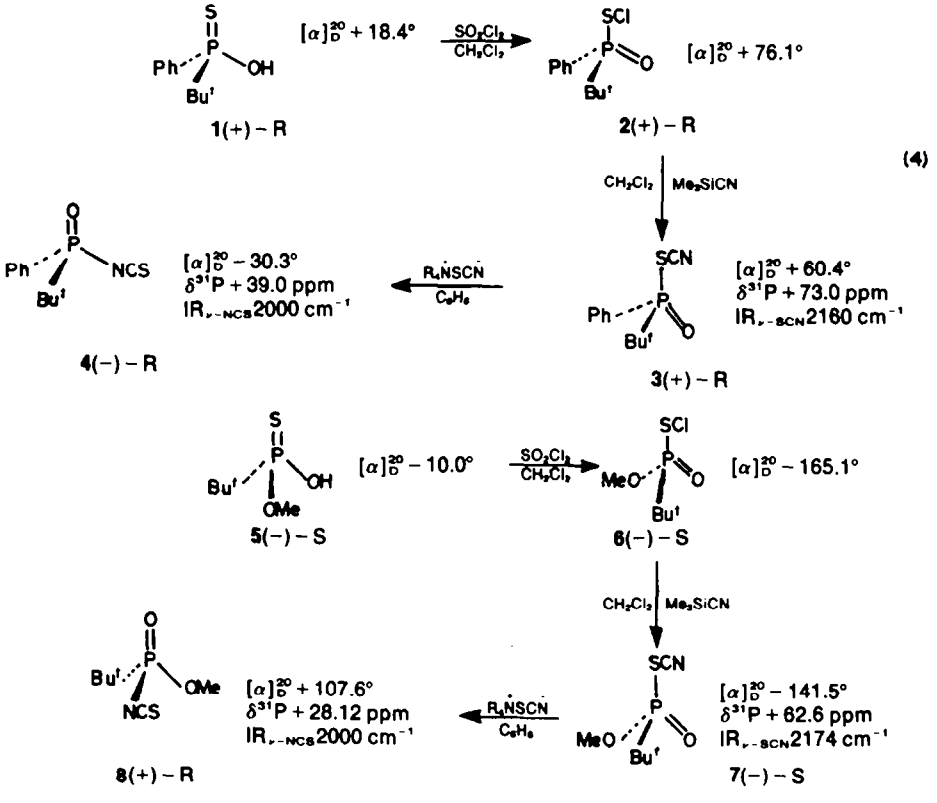
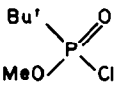


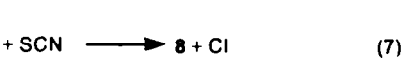
(4)

(5)

this the reactivity of the corresponding chloridate **10** is so low that direct nucleophilic displacement at P leading to isothiocyanidate **8** is impracticable. The only reason-



10

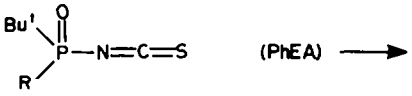


(7)

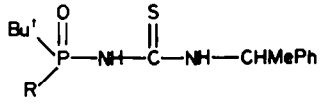
able method to obtain **8** can be based on the formation of **7** via the oxophosphoranesulphenylchloride **6** and subsequent isomerisation into **8**. This approach could be useful for other systems as a way to overcome difficulties connected with the low reactivity of some phosphorochloridates caused by both steric and electronic factors.

The stereoselectivity of the thiocyanidate-isothiocyanidate rearrangement The stereoselectivity of the rearrangement was determined by NMR spectroscopy which is based on the phenomena that diastereotopic nuclei are in principle anisochronous and should have different chemical shifts and coupling constants.[13]

We initially studied the thiourea derivatives **11** and **12** prepared from *R*-(+)-α-phenylethylamine (PhEA) and racemic isothiocyanidates **4** and **8** respectively.



4(R = Ph)
8(R = MeO) $[\alpha]_D^{20}$ + 39.9°



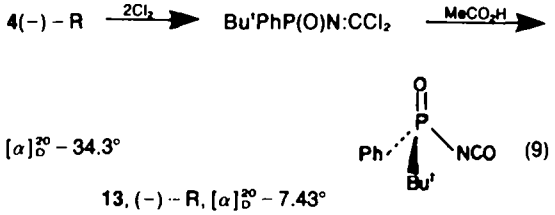
(8)

11(R = Ph); $[\alpha]_D^{20}$ + 5.1°, m.p. 170–171°
12(R = MeO); $[\alpha]_D^{20}$ + 36.6°, m.p. 136–137°

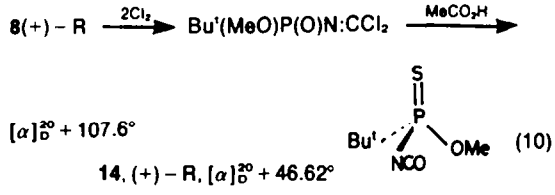
The ^{1}H NMR spectra of **11** and **12** in pyridine solution show indeed an anisochronism of the diastereotopic P–t-Bu and P–OMe groups. Two doublets of the same intensity were observed in both compounds. Similarly the ^{1}H heteronuclear decoupled ^{31}P NMR spectra of **11** and **12** showed two signals of equal intensity which are characteristic fro the presence of diastereotopic phosphorus nuclei. This observation was used to establish the enantiomeric purity of the chiral isothiocyanidates **4** and **8** after the thiocyanidate-isothiocyanidate isomerisation.

The observed chemical shift differences $\Delta\delta$ of the P–t-Bu, P–OMe groups (^{1}H NMR) and the P nuclei (^{31}P NMR) in the diastereoisomeric thioureas are shown in the Fig. 1. The optical purity of the rearranged isothiocyanidates **4** and **8** was determined directly from the integrated ^{1}H and ^{31}P NMR spectra of their reaction products **11** and **12** with (+)-*R*-PhEA which were prepared immediately after the isomerisation. Thus the thiourea **11** prepared from crude undistilled **4** ($[\alpha]_D^{20}$ −30.3°) and analyzed by ^{31}P NMR consisted of a mixture of two diastereoisomers: ^{31}Pδ + 42.14 ppm (86%) and ^{31}Pδ + 42.69 ppm (14%). The ratio of diastereoisomeric thioureas present in **11** was also calculated from the integrated proton signals of the P–t-Bu group. Considering that the optical purity of the starting thioic acid **1** was 76.5% [(+)-*R*] and, that the relative composition of diastereoisomeric thioureas **11** should correspond to those of *R*- and *S*- enantiomeric isothiocyanidates in **4** after rearrangement, the stereoselectivity of the isomerisation **3**→**4** catalysed by thiocyanate anion can safely be estimated as not lower than 97%. The small amount of reacmisation can be partly atributed to racemisation of the final product **4**. It is of interest to mention that the isolation of the diastereoisomeric pure thiourea **11**, ^{31}Pδ + 42.14 ppm, $[\alpha]_D^{20}$ + 90.2°, m.p. 158°, is readily accomplished by crystalization from chloroform-hexane. A similar picture was observed when thiocyanidate **7** rearranged into isothiocyanidate **8**. After reaction with (+)-*R*-PhEA a mixture of two diastereoisomeric thioureas **12** ^{31}Pδ + 37.22 ppm (92%) and ^{31}Pδ + 37.34 ppm (8%) respectively was detected. Crystallization of **12** from n-heptane gave the thiourea $[\alpha]_D^{20}$ + 147.5°, m.p. 164° in which the ratio of diastereoisomers is retained. The optical purity of the thioic acid **7** was 86.5% [(−)-S]. Therefore the stereoselectivity of the rearrangement **7**→**8** was estimated as 98%. Figure 1 show the ^{1}H and proton decoupled ^{31}P NMR spectra of thioureas **11** and **12**.

Stereochemical correlations. To establish the stereochemical correlations between **3**, **7** and their isomers **4**, **8** after thiocyanidate–isothiocyanidate rearrangement it was necessary to transform optically active isothiocyanidates **4** and **8** into compounds of known stereochemistry by a stereoselective sequence of reactions. The configurations of thiocyanidates **3** and **7** are the same as those of the starting thioic acids **1** and **5** respectively. Both the reactions of **1** and **5** and the conversion of **2** and **6** into **3** and **7** (reactions 4, 5) proceed without bond breaking and ligand methathesis at the P centre. With this in mind we have examined the reaction of isothiocyanidates **4** and **8** with elemental Cl in an effort to synthesize isocyanidates **15** and **16**, respectively.



(9)



(10)

The reaction of **4** and with elemental Cl resulted in the formation of **13** and **14** which upon further reaction with acetic acid or phosphorus pentoxide yielded optically active isocyanidates **15** and **16**. The reactions described above are adaptations of synthetic procedures described by Kirsanov *et al.*[14] on achiral models. The isocyanidates **15** and **16** are of the same configuration as those of isothiocyanidates **4** and **8** since reactions leading from **4** and **8** to **15** and **16** do not involve any bond breaking at P. Having to our disposal optically active **15** and **16** of the same configuration as isothiocyanidates **4** and **8** we elaborated another sequence of stereoselective reactions

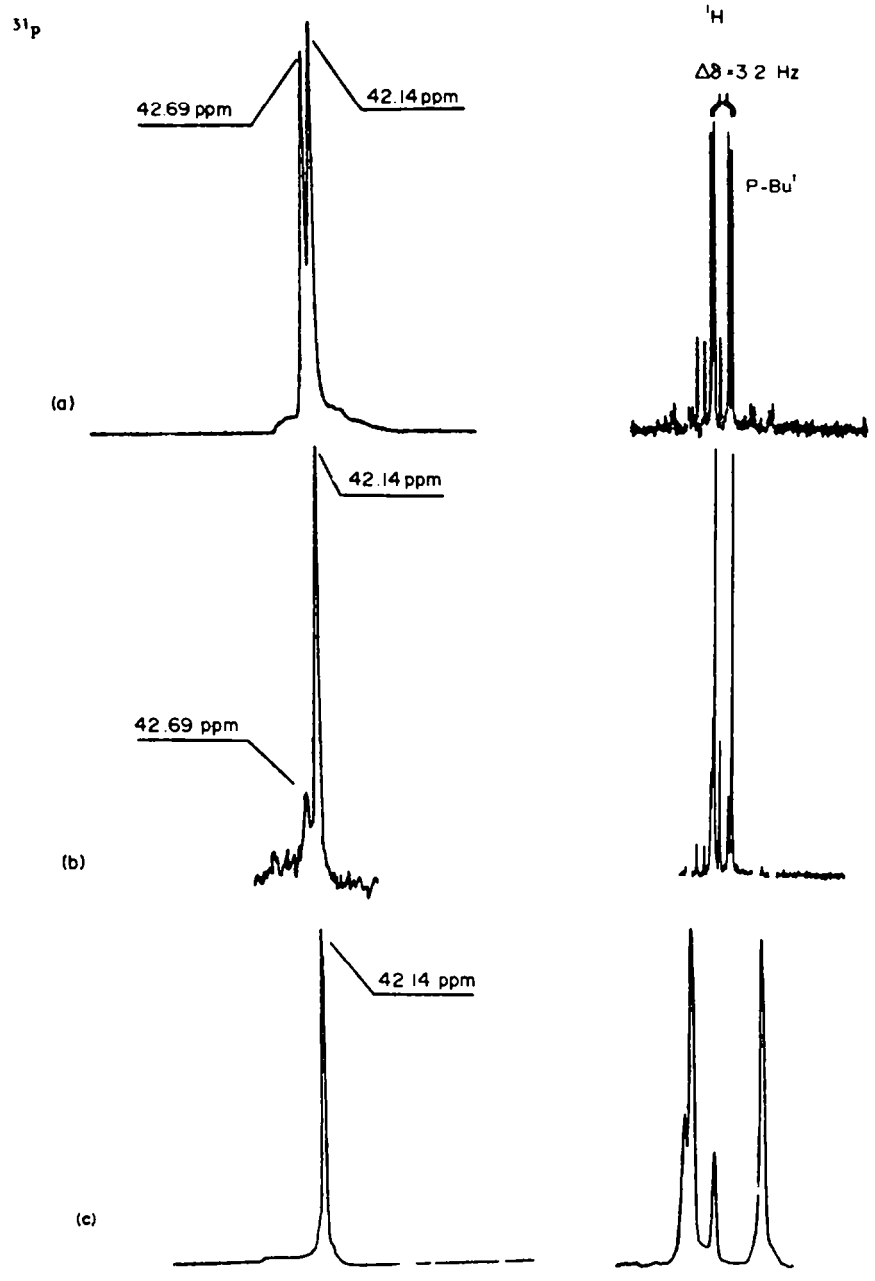

31P
42.69 ppm
42.14 ppm
(a)
1H
Δδ = 3.2 Hz
P-Bu'
42.14 ppm
42.69 ppm
(b)
42.14 ppm
(c)

Fig. 1(a).

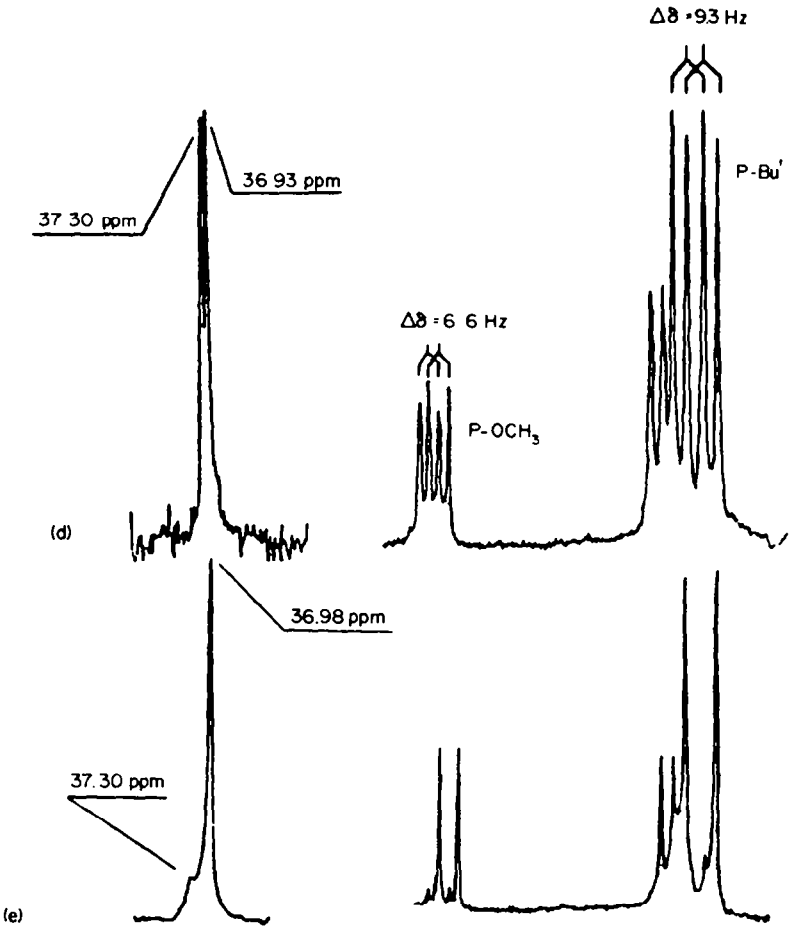
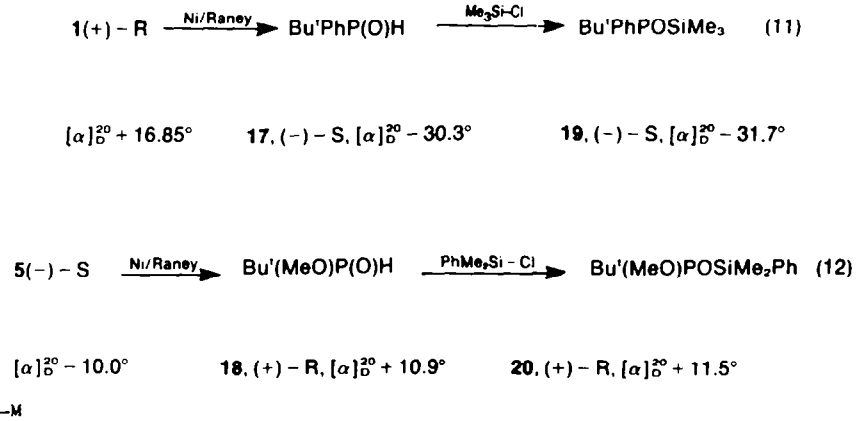


Fig. 1(b).

Fig. 1. (a) **11** $[\alpha]_D^{20}$ + 5. 1° from racemic **4**; (b) **11** from **4** $[\alpha]_D^{20}$ − 30.3°; (c) **11** one diastereoisomer; m.p. 158°, $[\alpha]_D^{20}$ + 90.2°; (d) **12** $[\alpha]_D^{20}$ + 36.6° from racemic **8**; (e) **12** from **8** $[\alpha]_D^{20}$ + 107.6°.

which correlate the starting monothioacids **1** and **5** with the isocyanidates **15** and **16**. The modothioacids **1** and **5** were reduced by Raney nickel into the corresponding phosphine oxides **17**[15] and **18**.[16] It has been previously establish in this Laboratory that the reduction proceeds with full retention of configuration.[15,16]

We took advantage of the possibility of transforming **17** and **18** into "true" tricoordinated phosphorus derivatives **19** and **20**. Retention of configuration in the silylation of phosphine oxides was earlier demonstrated by Benschop *et al.*[17] The silyl esters **19** and **20** undergo very smoothly a Staudinger reaction with t-butylazidofor-

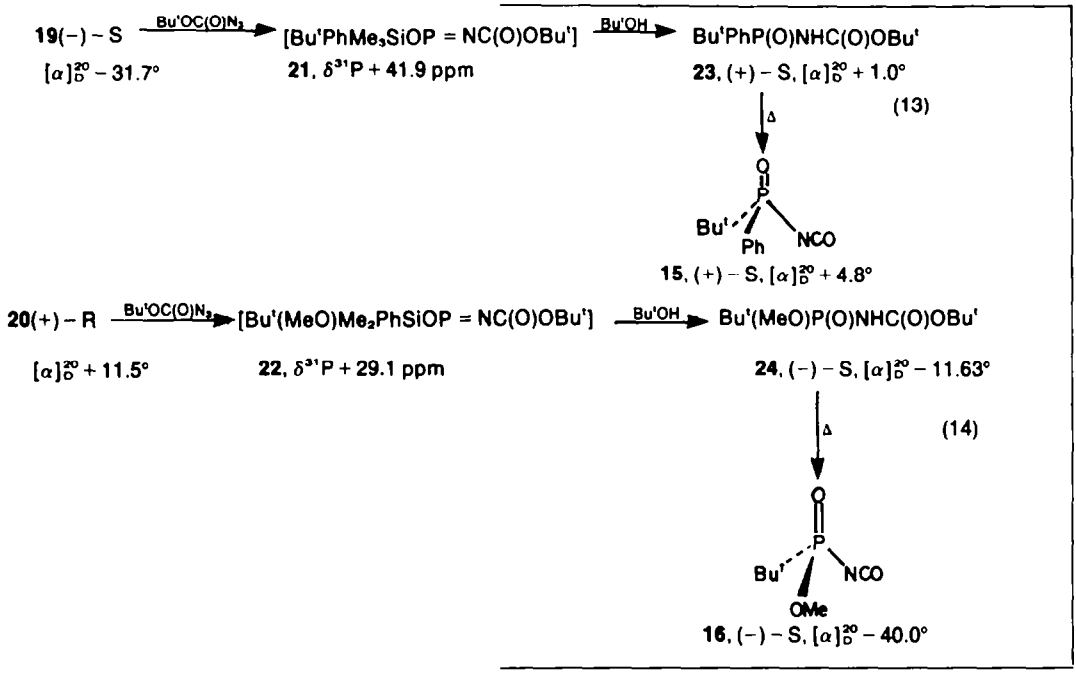


mate[18] to form the corresponding N - carbobutoxy - O - trimethylsilyl - t - butyl - phenyliminophosphinate **21** and N - carbobutoxy - O - dimethylphenylsilyl - t - butyl - O - methyliminophosphonate **22**.

DISCUSSION

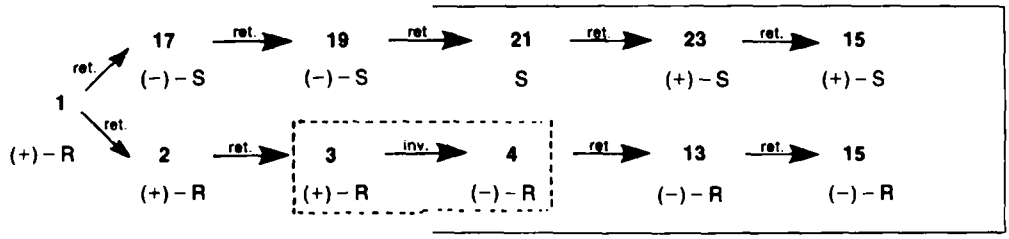
In principle three major mechanisms could be considered for the isomerisation of thiocyanidates $>P(O)-SCN \rightarrow >P(O)NCS$. There are: (a) Nucleophilic attack by the N-atom of thiocyanate ion on the phosphoryl centre; (b) Ionisation; (c) Free radical. The ionisation mechanism can be disregarded on general grounds and on the gasis of our experimental data. It is well established that in phosphorus chemistry there is no tendency in the condensed phase to form phosphacylium species $>\overset{+}{P}=O$ analogous to the acylium $>\overset{+}{C}=O$ or carbonium $\diagdown\!\!\diagup\overset{+}{C}$ cations.[21] Even under favourable structural circumstances in regards to electronic and steric effects for an ionic mechanism there is no evidence for its operation in solvolytic reaction at phosphoryl and thiophosphoryl centres.[22] The full inversion observed earlier in the isomerisation of cyclic systems[5] and now of acyclic ones described in this study speaks against the ionisation mechanisms. The radical dissociation in also unlikely for the following reasons. There is no influence of light on the rate of the isomerisation and no evidence for radical formation by CINDP technique.[23] In contrast the isomerisation is strongly catalyzed by P-nucleophiles.

Our results favour the first pathway to the isomerisation of thiocyanidates which becomes most evident in the presence of thiocyanate ions. This appears to be a direct nucleophilic displacement reaction at the P centre carried out by the N-end of the thiocyanate SCN^- ion with a trigonal bipyramide geometry transition state



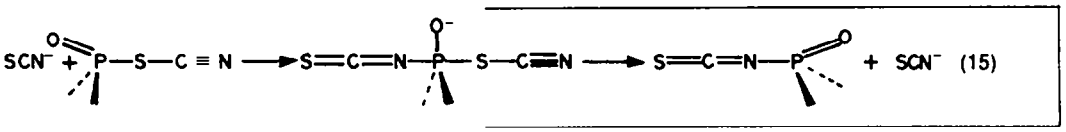
Both adducts **21** and **22** were not stable enough to be isolated and fully characterized. They were converted *in situ* into **23** and **24** by the action of t-butanol. Finally **23** and **24** were transformed into the optically active isocyanidates **15** and **16** by the thermal decomposition of **21** and **22** *in vacuo* at 80°–90°. This type of conversion of phosphorylated carbamates into isocyanidates was first reported for achiral compounds by Kirsanov *et al.*[19] There are good reasons to assume that Staudinger's reaction proceeds with retention of configuration at the phosphorus centre[20] as well as in the final elimination step leading to **15** and **16**.

As a consequence of these chemical transformations we were able to demonstrate that isocyanidates **15** and **16** prepared from the thioic acids **1** and **5** respectively, are of opposite sign in optical rotation compared with those synthesized directly from the isothiocyanidates **4** and **8**. Since isocyanidates **15** and **16**, prepared from thioic acids **1** and **5**, are of the same configuration as thiocyanidates **3** and **7** it can be firmly concluded that the *thiocyanidate-isothiocyanidate* isomerisation under discussion proceeds with inversion of configuration at the phosphorus centre. To clarify, the stereochemical correlations described above can be summarised in the following scheme:

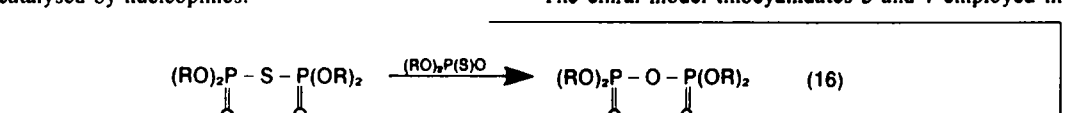


Analogous schemes can be presented for the family of stereo-selective reactions derived from the thioic acid **5** (−)-*S*.

$S_N2(P)$ or the addition–elimination mechanism with a short lived intermediates of the same geometry. We favour the former. This conclusion is based upon the full inversion observed and the facility of the rearrangement connected with the excellent leaving group-SCN departing with breaking of the P–S bond.

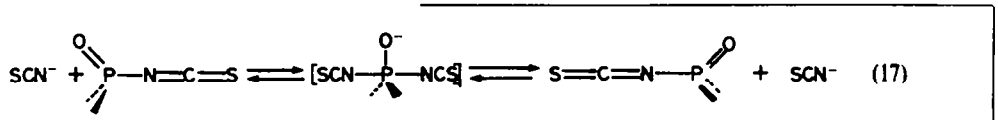


The facility of the *thiocyanidate–isothiocyanidate* isomerisation is definitely more pronounced for models which do not possess steric obstacles for nucleophilic attack by SCN^- anions. Without aid of the t-Bu or similar groups attached directly to the P atom it seems unrealistic to synthesize stable optically active thiocyanidates suitable for stereochemical studies. A somewhat lower rate of isomerisation of **7** in comparison with thiocyanidate **3** seems be reasonably explained by electronic effects. This is parralleled with the observed lower reactivity of Bu^t(MeO)P(O)X systems in comparison with Bu^{t}PhP(O)X for leaving group other than SCN^-. It is of interest to note that similar set of circumstances is observed in the case monothiopyrophosphates isomerisation catalysed by nucleophiles.



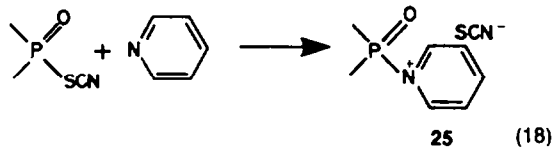
The racemisation of isothiocyanidates in the presence of SCN^- anions is dramatically slower than the corresponding isomerisation process of their precursors. This seems reasonable when one assumes that the isothiocyano (–N=C=S) leaving group is a poor leaving group in comparison with the isomeric thiocyano (–S–C≡N) group. This difference can satisfactorily be explained by tdhe higher strength of the P–N bond than that of the P–S bond. It seems that in phosphorus chemistry the -SCN group is among the best leaving groups. This property has some interesting synthetic applications. P-nucleophiles can efficiently displace the -SCN group in sterically hindered systems which are immune towards nucleophilic attack when other leaving groups are present.[24]

We propose the following mechanistic scheme for the racemisation of isothiocyanidates.



The formation of penta-coordinate intermediate is in this case more likely because of the relatively poor leaving group involved. This intermediate is symmetrical and collapses with the same propability into both enantiomers.

Finally a comment must be made of the sensitivity of thiocyanidates **3** and **7** towards tertiary amines as isomerisation catalysts, e.g. pyridine. It is most likely that the reaction with an amine provides an intermediate ion pair which becomes the primary source of SCN^- anions regenerated during the course of *thiocyanidate–isothiocyanidate* rearrangement. The concentration of the cationic species **25** should increase with increasing concentration of the amine involved. In consequence the parallel pathway for the isomerisation namely the attack of SCN^- anion on **25** should become of importance. With the reasonable assumption that the formation of **25**



25 (18)

occurs with net inversion of configuration as well as subsequent nucleophilic displacement by SCN^-. Final retention is to be expected relulting in racemisation of the isomerized product. Indeed when the *thiocyanidate–isothiocyanidate* rearrangements is carried out in pyridine medium extensive racemisation was observed.

CONCLUDING REMARKS

The chiral model thiocyanidates **3** and **7** employed in this study provided the expected detailed insight into the *thiocyanidate–isothiocyanidate* conversion. The fully stereoselective course of the isomerisation with inversion of configuration at the phosphorus in the presence of SCN^- anion clarify the nature of this reaction as a catalytic process involving a pentacoordinate transition state or intermediate. Thus this work generalizes our previous knowledge of *thiocyanidate–isothiocyanidate* rearrangement based on cyclic diastereoisomeric models.[5]

It is of interest to compare our results with the elegant studies of Fava *et al.*[25] on *thiocyanate–isothiocyanate* conversions in carbon chemistry. Such isomerisation occurs with net retention of configuration at the C atom accompanied by racemisation. The stereochemical and kinetic data of Fava provides strong evidence in favour of the mechanistic schemes involving ion pairs. This mode of isomerisation is definitely different of that observed in phosphorus chemistry.

EXPERIMENTAL

Solvent and commercial reagents were purified by conventional methods before use. All operations with P^{III} compounds were performed under dry N_2. ^1H NMR spectra were recorded on a Jeol-JNM60HL and JNM-FX60, Tesla BS-487C, and Perkin-Elmer R12B instruments with Me_4Si as internal standard. ^{31}P NMR spectra were measured with Jeol-JNM60HL, and JNM-FX60 Fourier transform spectrometers with 85%

H_3PO_4 as internal standard. The negative values ^{31}P shift correspond to compounds absorbing at higher fields than that of H_3PO_4. IR spectra of samples were recorded on UR-10 (Zeiss), Infracord 137 (Perkin–Elmer) and Specord 71 (Zeiss) spectrophotometers as thin films unless otherwise stated. Mass spectra were obtained on a LKB 9000 S spectrometer at 70 eV ionizing energy. Optical activity measurements were made with a Perkin–Elmer 141 photopolarimeter in benzene soln, unless specified otherwise. Acids **1** and **5** were synthesised and resolved into optical antipodes by known methods.[11,12,26] The optical purity of acids **1** and **5** were determined from the integrated spectra of their diastereoisomeric salts with (+)-*R*-α-phenylethylamine.[13] Other organophosphorus starting and or intermediate materials as the chlorides **9**[5] and **10**,[12] thiocyanidate **3**,[5] isothiocyanidates **4**[5] and **8**,[5] sulphenyl chloride **2**[5] were obtained by earlier reported methods. Cyanotrimethylsilane,[27] phenyldimethylchlorosilane[28] and benzyltri-n-butylammoniumthiocyanate[29] were prepared as described. t-Butylazidoformate was obtained from the reaction of HNO_3 with t-butylcarbazate according to Carpino,[18] yield 82%, b.p. 33–35°/35 mmHg. $n_D^{22} = 1.4230$ (lit.[18], b.p. 73–74°/70 mmHg, $n_D^{24} = 1.4227$.

The chlorination of (+)-R-**1**. Using a soln of (+) **1**, $[\alpha]_D^{20}$ +18.4° (MeOH) o.p. 76.5% (4.28 g; 0.02 mole) in 15 ml CH_2Cl_2 and sulphenyl chloride (0.68 g; 0.02 mole) in a conventional procedure 4.9 g of a yellow oil (+)-R-**2** $[\alpha]_D^{20}$ +76.1°, ^{31}P NMR +67.0 pm (CH_2Cl_2) was obtained. The crude (+)-*R*-**S 2** was immediately used for further reaction.

Reaction of (+)-R-**2** *with trimethylsilylcyanide.* Into the soln of (+)-R-**2** (4.3 g; 0.017 mole), $[\alpha]_D^{20}$ +76.1 in 20 ml CH_2Cl_2 trimethylsilylcyanide (2.5 g; 0.025 mole) was added dropwise with stirring at 0–2°. Stirring was continued at 5–8° until the yellow colour of **2** disappeared. The solvent Me_3SiCl and excess Me_3SiCN were removed under reduced pressure 0.1 mmHg/bath 0–5°. The white solid (+)-*R*- **3** was obtained from hexane. $[\alpha]_D^{20}$ +60.4°. ^{31}P NMR +73.8 ppm (CH_2Cl_2). IR (Nujol) 2160 (−SCN).

The reaction of racemic t-butylphenylphosphinoisothiocyanidate **4** *with* R(+) *α-phenylethylamine.* To the soln of PhEA $[\alpha]_D^{20}$ +39.0° (1.21 g; 0.01 mole) in 30 ml $CHCl_3$ (2.4 g; 0.01 mole) racemic **4** was added at −5° with stirring in 10 ml $CHCl_3$. Stirring was continued for 1 hr at 15°. The chloroform soln of the crude product was washed with a chilled 1% of HClaq (10 ml), water (10 ml), 1% $KHCO_3$aq (10 ml) and again with water (5 ml) and dried over $MgSO_4$. The solvent was evaporated and residual solid recrystallised from n-heptane, yield 3.3 g (95%), white needles m.p. 170–171°. $[\alpha]_D^{20}$ + 5.1° (EtOH). ^{31}P NMR $\delta_1 = +42.69$ ppm and $\delta_2 = +42.14$ ppm (C_6H_5N) intensity 1:1. ^1H NMR ($CDCl_3$) $\delta = 1.13$ ppm (d. Bu^t), $\delta = 1.23$ (d. Bu^t) twice doublet intensity 1:1, $^3J_{PH} = 16$ Hz, $\delta = 1.42$ (d. C–CH_3), $\delta = 5.6$ (q. H), $\delta = 7.5$ (m. C_6H_5). (Found: C, 63.3; H, 7.2; N, 7.4; P, 9.0. Calc. for $C_{19}H_{25}NO_2PS$: C, 63.3; H, 6.9; N, 7.7; P, 8.6). The product was identified as a 1:1 mixture of diastereoisomeric **11**.

The rearrangement of (+)-R-**3** *in the presence of benzyltri-n-butylammonium thiocyanate.* To a soln of benzyltri-n-butylammonium thiocyanate (0.02 g) in 20 ml C_6H_6 **3** $[\alpha]_D^{20}$ + 60.4 (0.27 g; 0.001 mole) was added at 20° and placed immediately in the measuring tube of the polarimeter apparatus. After *ca* 3.5 min the optical rotation $[\alpha]_D^{20}$ −30.3° was observed. The ^{31}P NMR and IR spectra recorded show a signal at $^{31}P\delta = +39.6$ ppm and absorption bond $IR_{\nu\text{-NCS}}$ 2000 cm^{-1} characteristic for the rearranged product **4**. The crude product of **4** $[\alpha]_D^{20}$ −30.3° with (+) PhEA in pyridine analysed by ^{31}P NMR showed two signal $\delta_1 = +42.14$ ppm (86%) and $\delta_2 = +42.69$ ppm (14%). ^1H NMR ($CDCl_3$) $\delta = 1.13$ ppm (d. Bu^t) (87%) $\delta = 1.23$ (d. Bu^t) 13%. Fractional crystallisation of crude **11** from chloroform–ligroin (60°–80°) gave a diastereoisomeric pure sample of **11**, m.p. 158°. $\delta = +42.14$ ppm (C_5H_5N): $[\alpha]_D^{20}$ +90.2 (EtOH): ^1H NMR ($CDCl_3$), $\delta = 1.13$ ppm (d, Bu^t) $^3J_{Ph} = 16$ Hz, $\delta = 1.42$ (d. C–CH_3) $^3J_{HCCH_3} = 7$ Hz, $\delta = 7.4 - 7.6$ ppm (m. C_6H_6). MS *m/e*: 18 (100%), 41 (78%), 57 (35%), 77 (32%), 106 (72%), 125 (100%), 183 (96%), 360 (4%) (M^+).

The rearrangement of (+)-R-**3** *in the presence of pyridine.* To a soln of **3** (1.24 g; 7.5×10^{-4} mole) $[\alpha]_D^{20}$ +60.4° in 15 ml CH_2Cl_2 two drops of anhyd pyridine were added. The mixture was allowed to stand at room temp for 15 min. The ^{31}P NMR spectra showed after this time only a signal at $\delta = +39.6$ ppm characteristic of **4**. The products of **4** with (+) PhEA was a mixture of diastereoisomeric **11** ^{31}P NMR $\delta_1 = +42.14$ ppm (84%), $\delta_2 = +42.69$ ppm (16%) which was confirm by ^1H NMR.

The chlorination of (−)-S **5**. The reaction of **5** (4.0 g; 0.023 mole) $[\alpha]_D^{20}$ −9.98° o.p. 86.5% with sulphurylchloride (3.2 g; 0.023 mole) at 0–5° in 20 ml CH_2Cl_2 gave (−)-*S*-**6**, yield 4.5 g (96%); b.p. 54°/0.35 mmHg, $[\alpha]_D^{20}$ −165.12°, ^{31}P NMR $\delta = +63.5$ ppm (CH_2Cl_2).

(−)-S-*t-butyl*-O-*methylphosphonothiocyanidate* **7**. According to the procedure described for **3**, **7** was synthesised from Me_3SiCN (2.5 g; 0.025 mole) and **6** (4.0 g; 0.019 mole) $[\alpha]_D^{20}$ −165.12° in CH_2Cl_2 (20 ml), yield 3.1 g (85%), b.p. 57–57°/0.1 mmHg, $[\alpha]_D^{20}$ −141.6°, ^{31}P NMR $\delta = +62.6$ ppm. IR (neat) 2174 (-SCN), 1272 (P=O). (Found: C, 37.6; H, 6.3; N, 7.3; P, 15.9. Calc. for $C_6H_{12}NO_2PS$: C, 37.3; H, 6.25; N, 7.25; P, 16.03%).

Reaction of racemic t-butyl-O-methylphosphonoisothiocyanidate **8** *with* R-(+)-α-PhEA. Using the procedure described for **11** from racemic **8** (1.9 g; 0.01 mole) and (1.2 g; 0.01 mole), PhEA $[\alpha]_D^{20}$ +39.0° **12** was obtained, yield 2.8 g (90%), m.p. 136–137° (heptane), $[\alpha]_D^{20}$ + 36.64° (EtOH). ^{31}P NMR $\delta_1 = +37.22$ ppm, $\delta_2 = +37.34$ ppm (C_5H_6N) intensity 1:1. ^1H NMR (C_5H_5N) $\delta = 1.13$ ppm (d. Bu^t) and $\delta = 1.27$ ppm (d. Bu^t) intensity 1:1. $^3J_{PH} = 17.3$ Hz, $\delta = 1.75$ ppm (d. C–CH_3) $^3J_{C\text{-}CH_3} = 7.36$ Hz, $\delta = 3.58$ ppm (d. –OCH_3) and $\delta = 3.68$ ppm (d. –OCH_3) intensity 1:1 $^3J_{POCH_3} = 11.3$ Hz, $\delta = 5.75$ ppm (q. H). (Found: C, 53.25; H, 7.40; N, 7.42; N, 9.12; P, 9.75. Calc. for $C_{14}H_{23}N_2O_2PS$: C, 53.48; H, 7.37; N, 8.91; P, 9.85%). The product was a mixture of the diastereoisomeric **12**.

The rearrangement of (−)-S-**7** *in the presence benzyltri-n-butylammonium thiocyanate.* To a soln of (−)-*S*-**7** $[\alpha]_D^{20}$ −141.6° (2.97 g; 0.0153 mole) in 20 ml C_6H_6 was treated at 20° with a soln of benzyltri-n-butylammonium thiocyanate (0.25 g). Monitoring the ^{31}P NMR spectra and optical rotation the solution showed complete isomerisation of (−)-**7** after 33 min, yielding **8**, $[\alpha]_D^{20}$ +107.6°, b.p. 58°/0.1 mmHg, 2.4 g (82%). ^{31}P NMR $\delta = +28.12$ ppm (neat), IR (film) 1220 (P=O), 2000 (−NCS). ^1H NMR (CCl_4), $\delta = 1.2$ ppm (d. Bu^t), $^3J_{PH} = 18$ Hz, $\delta = 3.7$ ppm (d. OCH_3), $^3J_{PH} = 12$ Hz. (Found: C, 37.4; H, 6.9; N, 6.2; P, 15.1. Calc. for $C_6H_{12}NO_2PS$: C, 37.2; H, 6.2; N, 7.2; P, 16.0%).

A sample of **8** (0.5 g; 0.0025 mole) $[\alpha]_D^{20}$ +107.6° was treated in $CHCl_3$ (15 ml) with *R*(+)-PhEA (0.31 g; 0.0025 mole). The solvent was removed *in vacuo* and the residual crude **12** was dissolved in pyridine and examined by ^{31}P and ^1H NMR. ^{31}P NMR $\delta_1 = +36.98$ ppm (92%), $\delta_2 = +37.30$ ppm (8%). ^1H NMR $\delta_1 = 1.13$ ppm (d. Bu^t), $\delta_2 = 1.27$ ppm (d. Bu^t) intensity 92:8, $\delta_1 = 3.58$ ppm (d. OCH_3), $\delta_2 = 3.68$ ppm (d. OCH_3) intensity 92:8. Crude **12** was recrystallised from n-heptane m.p. 162–164°. $[\alpha]_D^{20}$ +147.55° (EtOH). The relative intensity of ^{31}P and ^1H NMR signals was retained.

Rearrangement of (−)-S-**7** *in the presence of pyridine.* To **1** (3.5 g; 0.0175 mole) $[\alpha]_D^{20}$ −140.0° two drops of anhyd pyridine were added. The distillation of this mixture gave **8** $[\alpha]_D^{20}$ +104.0° 2.5 g (83%), b.p. 57–58°/0.1 mmHg. ^{31}P NMR $\delta = +29.0$ ppm (CH_2Cl_2). Thiourea **12** obtained from **8** $[\alpha]_D^{20}$ +104.0° was a mixture two diastereoisomers in ratio 90:10 by ^{31}P and ^1H NMR.

The reaction of (+)-*t-butylphenylphosphinochloridate* **9** *with potassium thiocyanide.* A soln of **9** (2.1 g; 0.01 mole) $[\alpha]_D^{20}$ +31.7° and KCCN (1.1 g; 0.01 mole) in acetone (20 ml) was heated under reflux for 2 hr. The solvent was removed *in vacuo* (15 mmHg, 15° both temp.) and 150 ml benzene was added. The solid KCl was removed by centrifugation and the solvent evaporated. Fully racemic **4** was obtained, ^{31}P NMR $\delta = +39.0$ (CH_2Cl_2) $[\alpha]_D^{20}$ 0°.

The attempts of reaction of (±) *t-butyl-O-methylphosphonochloridate* **10** *with potassium thiocyanate.* A soln of **10**[12] (1.7 g; 0.01 mole) and KSCN (1.11 g; 0.011 mole) in acetonitrile (20 ml) was heated under reflux for 16 hr. About 90% of starting **10** along with *ca* 10% unidentified decomposition products were observed by ^{31}P NMR.

The chlorination of (−)-R-**4**. Through a soln of (−)-*R*-**4** (2.0 g; 0.008 mole) $[\alpha]_D^{20}$ −30.3° in 10 ml anhyd CCl_4 dry Cl_2 was passed at −10° until the exothermic reaction subsided. The excess chlorine, sulphur chloride and CCl_4 were removed *in*

vacuo. The residual yellow oil of **13** was purified by distillation, yield 2.1 g (90%), b.p. 90–92°/0.002 mmHg, $[\alpha]_D^{20}$ −7.43°. ^{31}P NMR δ = + 39.4 ppm (CH_2Cl_2). IR ($CHCl_3$) 1650, 1735 (–N=CCl$_2$), 1230 (P=O). (Found: C, 47.30; H, 4.40; N, 4.85; P, 11.10. Calc. for $C_{11}H_{14}Cl_2NOP$: C, 47.50; H, 5.07; P, 11.14; N, 5.02%).

The reaction of (−)-R-**13** *with acetic acid.* A soln of **13** (1.2 g; 0.004 mole) $[\alpha]_D^{20}$ −7.43°, 3 ml anhyd-AcOH and 20 ml benzene was heated under reflux for 5 hr. The solvent, excess AcOH, AcCl and the remaining gaseous Hcl was removed *in vacuo*. The crude **15** was purified by distillation, b.p. 81–83°/0.1 mnHg, n_D^{26} = 1.5360, $[\alpha]_D^{20}$ −9.33°. ^{31}P NMR −40.4 ppm, yield 0.7 g (80%). IR (film) 1225 (P=O), 2250 (–NCO). (Found: C, 58.4; H, 6.4; N, 5.9; P, 13.7. Calc. for $C_{11}H_{14}NO_2P$: C, 59.2; H, 6.3; N, 6.3; P, 13.9%).

Chlorination of (+)-R-**8**. We adapt the procedure used for **4**, and with the aid of a small amount of powdered $AlCl_3$ as catalyst from (+)-*R*-**8** $[\alpha]_D^{20}$ +107.6° (2.0 g; 0.01 mole) (+)-*R*-**14** (1.8 g; 87%) b.p. 46–47°/0.05 mmHg, n_D^{26} 1.4800, $[\alpha]_D^{20}$ +46.62° was obtained. ^{31}P NMR δ = + 34.5 ppm (neat). IR (film) 1248 (P=O), 1650, 1732 (–N=CCl$_2$). (Found: C, 30.5; H, 5.0; N, 5.9; P, 13.00. Calc. for $C_6H_{12}Cl_2NO_2P$: C, 31.05; H, 5.21; N, 6.03; P, 13.34%).

The reaction of (+)-R-**14** *with acetic acid.* Using the conditions described for **13**, the reaction between (+)-*R*-**14**, (1.5 g; 0.006 mole) $[\alpha]_D^{20}$ +46.62° and AcOH (3 ml) gave (+)-*R*-**16** (0.9 g; 80%) b.p. 26–28°/0.025 mmHg, n_D^{24} = 1.4428, $[\alpha]_D^{20}$ +40.0°. ^{31}P NMR δ = + 30.4 ppm (neat). IR (film) 1265 (P=O), 2284 (–NCO). MS *m/e*: 41 (53%), 57 (100%), 79 (24%), 121 (94%), 151 (16%), 177 (8%) (M^+).

Optically active t-butylphenylphosphine oxide **17**. To a refluxing solution of **1** (12.6 g; 0.058 mole) $[\alpha]_D^{20}$ +16.85° in 100 ml EtOH, a suspension of freshly prepared Raney-Ni (30 g) was added portionwise over a period of 10 hr. The mixture was filtered, the solvent evaporated *in vacuo* and the residual oil of the (−)-*R*-**17** was purified by distillation, yield 8, 8 g (82%), b.p. 95–96°/1 mmHg. $[\alpha]_D^{20}$ −30.3°, ^{31}P NMR δ = + 42.0 ppm (C_6H_6).

The synthesis of (−)-S-*t-butyltrimethylsilylphenylphosphinate* **19**. To a soln of **17** (8.0 g; 0.043 mole) $[\alpha]_D^{20}$ −30.3° and Et_3N (4.45 g; 0.044 mole) in 10 ml C_6H_6, chlortrimethylsilane (8.7 g; 0.08 mole) in 10 ml C_6H_6 was added with stirring at 15–20°. After addition the mixture was heated with stirring to 45–50° for 2 hr. The amine salt was filtered off solvent was removed *in vacuo* and residual liquid was distilled, yielding **19** (8.3 g; 80%), b.p. 48°/0.1 mmHg, n_D^{20} = 1.4964. $[\alpha]_D^{20}$ − 31.8°. ^{31}P NMR δ = + 112.1 ppm (CH_2Cl_2).

The condensation of (−)-S-**19** *with t-butylazidoformate.* A soln of t-butylazidoformate (1.14 g; 0.008 mole) in 10 ml Et_2O was added with stirring at 10° into a soln of **19** (1.5 g; 0.006 mole) $[\alpha]_D^{20}$ −31.8° in 20 ml Et_2O. Evolution of N_2 was immediately observed. Stirring was continued for 2 hr. Solvent and excess azide was removed *in vacuo* and the remaining oil of **21** ^{31}P NMR δ = + 41.9 ppm (Et_2O) was used immediately for further reaction.

The synthesis of optically active t-butylphenylphosphinoisocyanidate (+)-S-**15** *from* **21**. A soln of freshly prepared **21** (2.0 g; 0.005 mole) in 20 ml C_6H_6 was heated 2 hr under reflux with 5 ml t-BuOH. The solvent was removed *in vacuo* and crude **23** was obtained as a solid, yield 1.2 g (80%), $[\alpha]_D^{20}$ +1.0°. ^{31}P NMR δ = + 33.0 ppm (C_6H_6). (Found: C, 60.23, H, 7.72; N, 5.61; P, 10.10. Calc. for $C_{15}H_{24}NO_3P$: C, 60.59; H, 8.13; N, 4.7; P, 10.42%). Crude **23** (1.2 g) $[\alpha]_D^{20}$ +1.0° was placed in a distillation apparatus and heated on an oil bath to 135° *in vacuo* 0.1 mmHg, yielding (+)-*S*-**15** (0.63 g; 70%). $[\alpha]_D^{20}$ +4.8°. ^{31}P NMR δ = + 39 ppm (C_6H_6).

Reduction of (−)-S-**5** *with Raney-nickel.* According to a procedure described for the synthesis of (−)-*S*-**17**, from (−)-*S*-**5** (12.3 g; 0.073 mole) $[\alpha]_D^{20}$ −10.0° and Raney-nickel (25 g), **18** (7.9 g; 80%) was obtained, b.p. 87°/35 mmHg. $[\alpha]_D^{20}$ +10.9° (neat). ^{31}P NMR δ = + 48.7 ppm (neat).

Reaction of (+)-R-**18** *with dimethylphenylchlorosilane.* In the manner described for **19**, **18** was obtained from (+)-*R*-**18** (7.0 g; 0.05 mole) $[\alpha]_D^{20}$ +10.9° and dimethylphenylchlorosilane (8.5 g; 0.05 mole) in the presence of Et_3N (5.05 g; 0.05 mole) in benzene, yield 9.0 g (65%), b.p. 58–60°/ 0.05 mmHg. $[\alpha]_D^{20}$ +11.52° (neat), ^{31}P NMR δ = + 175.9 ppm (neat).

Reaction of (+)-R-**20** *with t-butylazidoformate.* The condensation of **20** (6.0 g; 0.021 mole) $[\alpha]_D^{20}$ +11.52° with azide (4.3 g; 0.03 mole) in 30 ml Et_2O, gave 8.0 g of a crude oil product identified as **22** ^{31}P NMR δ = + 29.1 ppm (Et_2O) which was used immediately for the synthesis of **16**.

The synthesis of (−)-S-*t-butyl-O-methylphosphonoisocyanidate* **16** *from* **22**. Into a soln of crude **22** (7.0 g; 0.018 mole) in 15 ml Et_2O, t-BuOH 1 g was added. The mixture was refluxed for 6 hr and evaporated after cooling to rt under reduced pressure 0.05 mmHg for 5 hr. An oil, (4.5 g), identified as **24** $[\alpha]_D^{20}$ −11.63. ^{31}P NMR δ = + 36.1 ppm (C_6H_6), was obtained. Crude **24** (4.0 g) was kept in a distillation apparatus heated by an oil bath at temp. 80° under pressure 0.1 mmHg. After 2.5 hr 3.2 g of product, b.p. 65–73°, was collected. Redistillation gave 2.8 g b.p. 30–32°/0.003 mmHg (−)-*S* **16**, $[\alpha]_D^{20}$ −40.0°. ^{31}P NMR δ = + 30.7 ppm (C_6H_6). The condensation of **16** $[\alpha]_D^{20}$ −40.0° with aniline gave N-t-butyl-O-methylphosphono-N'-Phenylurea, m.p. 168–171°. $[\alpha]_D^{20}$ −16.0°. ^{31}P NMR δ = + 37.5 ppm ($CHCl_3$).

The rearrangement of (−)-S-*t-butylphenylphosphinothiocyanidate in pyridine.* A soln of (−)-*S*-**3** (0.7 g) $[\alpha]_D$ −88.4° in 3 ml CH_2Cl_2 was added in one portion to vigorously stirred pyridine (25 ml) at 20°. The rearrangement of **3** into **4** took place immediately. Only one signal at ^{31}P NMR δ = + 39.0 ppm was observed. A sample of this pyridine soln containing **4** was treated with *R*-(+)-α-PhEA. Two ^{31}P NMR signals δ_1 = 42.14 ppm and δ_2 = + 42.69 ppm in the ratio 53:47 were observed indicating the presence of nearly racemic **11**.

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