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OPTICALLY ACTIVE TRIVALENT PHOSPHORUS COMPOUNDS—I

DIASTEREOISOMERIC O-MENTHYL ETHYLPHENYLPHOSPHINITES: SYNTHESIS, CHIRALITY AT PHOSPHORUS AND STEREOCHEMISTRY OF NUCLEOPHILIC DISPLACEMENT REACTION

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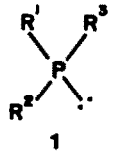
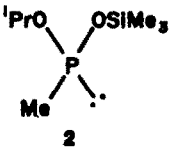
Abstract—The reaction between racemic ethylphenylchlorophosphine and menthol has been found to give a mixture of diastereoisomeric O-menthyl ethylphenylphosphinites (4) in unequal ratio. The diastereoisomeric content depends mainly on the tertiary amine used for the condensation. The chirality at phosphorus in the diastereoisomeric esters (4a and 4b) has been assigned by means of chemical correlation (conversion into optically active methylethylphenylphosphine oxide) and proton NMR spectra. It has been demonstrated that nucleophilic substitution at phosphorus in 4 occurs with inversion of configuration.

Trigonal pyramidal, three-coordinate phosphorus compounds with three different ligands are chiral at phosphorus and can in principle be resolved into enantiomers or prepared in optically active forms. For a long time the only compounds known belonging to the optically active P^{III} compounds were optically active tertiary phosphines (1), first prepared by Horner[1] in 1961. In 1971 Benschop *et al.*[2] have synthesized optically active O-trimethylsilyl O-isopropyl methylphosphonite (2), the first example of an optically active trivalent phosphorus compound containing a phosphorus-oxygen bond. However, the ester 2 was unsuitable for studies on organophosphorus reaction mechanisms since nucleophilic reagents prefer to react at silicon rather than phosphorus.



1

R = alkyl, aryl



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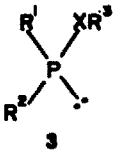
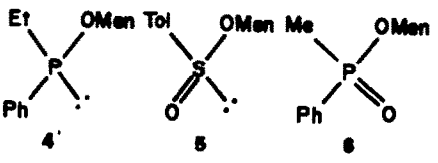


3

R = alkyl, aryl
X = O, S

Very recently we reported[3,4] a general approach to simple, optically active trivalent phosphorus esters (3) based on asymmetric reaction between chiral P^{III} chlorides and achiral alcohols or thiols in the presence of optically active tertiary amines. The optically active esters (3) were subsequently used[4] to establish the stereochemistry of nucleophilic substitution at the optically active trivalent P atom.

As part of our program on the optically active trivalent P compounds we now report the results of the study on diastereomeric O-menthyl ethylphenylphosphinites (4) which contain chirality centres at phosphorus and in the menthyl moiety. The latter was chosen in our investigations in view of the fact that diastereomeric menthyl *p*-toluenesulphinate (5)[5] and menthyl methylphenylphosphinate (6)[6] are the main precursors to many optically active compounds with the sulphur and phosphorus atom as a sole chirality centres.

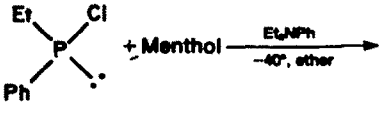


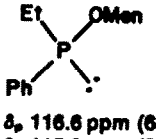
4 5 6

OMen = (−)-menthoxy

RESULTS AND DISCUSSION

Synthesis of diastereoisomeric O-menthyl ethylphenylphosphinites (4). We found that treatment of racemic ethylphenylchlorophosphine with menthol in ether solution at −40 to −30° in the presence of N,N-diethylaniline resulted in the formation of a mixture of the diastereoisomeric esters (4a and 4b) in a ratio 68:32 as determined by ^{31}P NMR spectroscopy.





4a: δ_P 116.6 ppm (68%)
4b: δ_P 115.0 ppm (32%)

As expected, this type of asymmetric condensation afforded a mixture of the diastereoisomeric esters (4) the ratio of which is most likely controlled by kinetic factors since distillation of the reaction product at 130–140° resulted in the formation of an equimolar mixture of 4a and 4b. It was also observed that epimerisation at P in 4 is caused by amine hydrochloride which is sparingly soluble in the reaction product. Therefore, in order to obtain the ester (4) of high diastereoisomeric purity it is necessary to remove as good as possible the traces of amine hydrochloride.

In this context, it is interesting to note that a tertiary amine used for the condensation shown above has an important influence on the stereochemistry of this simple reaction. As it is seen from the results summarised in Table 1 it affects not only the diastereoisomeric purity of 4 but also the chirality at P of the major diastereoisomer formed. The highest diastereoisomeric purity was observed when triethylamine was used as a tertiary amine. In this case, however, the ester (4b) was formed as a predominant isomer. These results tend to support the view that a tertiary amine acts not only as a simple hydrogen chloride acceptor but it must participate in the reaction mechanism.

Chemical assignment of chirality at phosphorus in diastereoisomeric esters (4). The chirality at P in the diastereoisomeric esters (4a and 4b) follows from chemical correlation with optically active methylethylphenylphosphine oxide shown in Scheme 1 and 2. In the first step, a mixture of 4a and 4b [60:40] was treated with sulphur to give a mixture of the corresponding O-menthyl ethylphenylphosphinothionates (7) in the same ratio (^{31}P NMR assay).

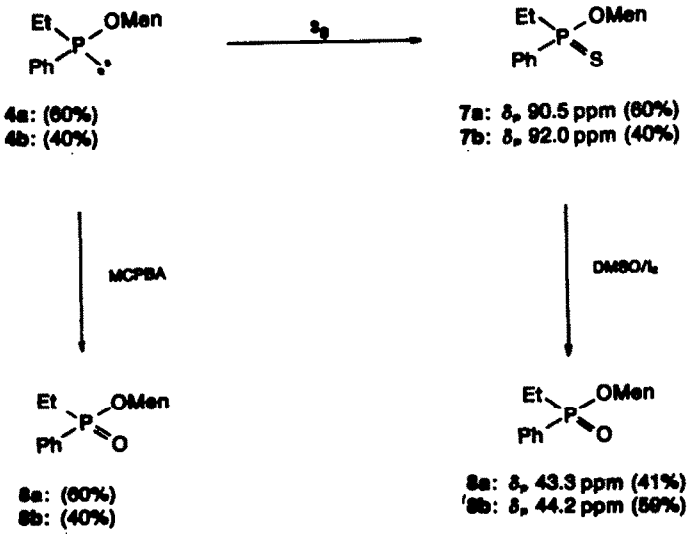
By fractional crystallisation from ethyl acetate we were able to isolate in a good yield one pure isomer 7a, $[\alpha]_{589} - 49.5°$, which on treatment with dimethylsulphoxide in the presence of iodine was converted into (−)-O-menthyl ethylphenylphosphinate (8b), $[\alpha]_{589} -$ 54.3°.† The latter was in turn reacted with methyl magnesium iodide to afford (−)-methylethylphenylphosphine oxide (9), $[\alpha]_{589} - 18.1°$.

If one takes into account that the absolute configuration of (−)-(9) is *S*[6] and the conversion (−)-(8b)→ (−)-(9) is accompanied by inversion at P[6] it follows that the *S* configuration should be assigned to (−)-phosphinate (8b).

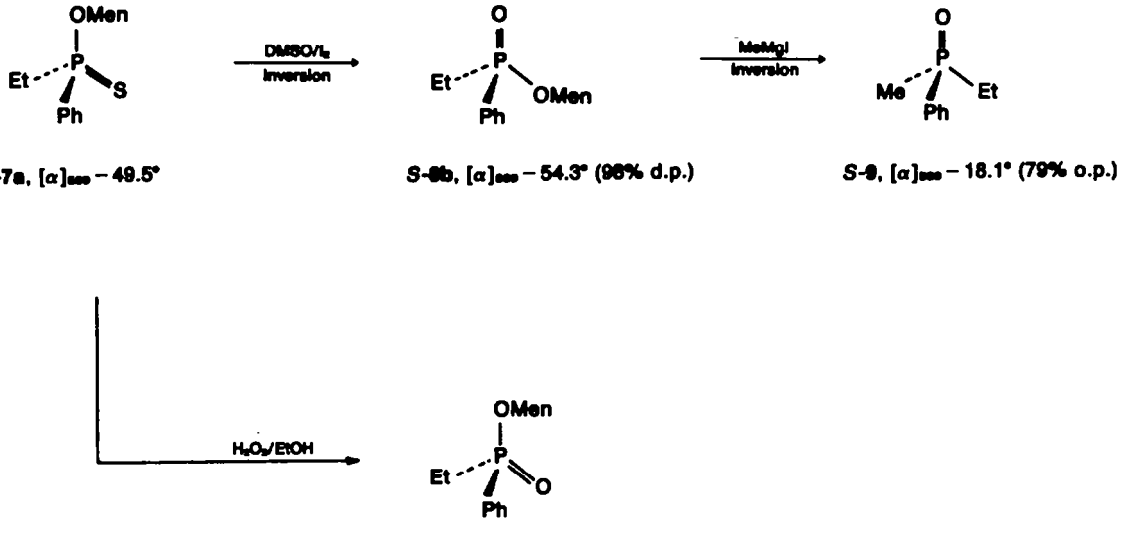
†It was found that oxidation of 7a with H_2O_2 in ethanol afforded a mixture of the diastereoisomeric phosphinates (8a and 8b) in a ratio 86:14. Thus, the conversion →P=S⟶→P=O occurred with predominant retention at phosphorus. When *m*-chloroperbenzoic acid was used for the same purpose a mixture of 8a and 8b was formed in a ratio 54:46.

Table 1. The influence of tertiary amine and solvent on the diastereomeric content of O-menthyl ethylphenylphosphinites (4)

Amine	4a (%)	4b (%)	Solvent
Et_2NPh	68	32	Et_2O
Et_3N	29	71	Et_2O
(+) $Me_2NCH(Me)Ph$	40	60	Et_2O
(−) $Me_2NCH(Me)Ph$	41	59	Et_2O
Et_2NPh	57.5	42.5	Petr.ether
Et_2NPh	60	40	CH_2Cl_2
Et_2NPh	43	57	THF



Scheme 1.



S-7a, $[\alpha]_{589}$ − 49.5°

S-8b, $[\alpha]_{589}$ − 54.3° (98% d.p.)

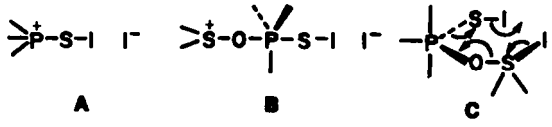
S-9, $[\alpha]_{589}$ − 18.1° (79% o.p.)

R-8a, $[\alpha]_{589}$ − 24.5° (86% d.p.)

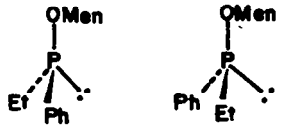
Scheme 2.

In order to establish the steric course of the oxidation of (−)-(7a) by means of DMSO/I_2-reagent some additional experiments were carried out. Thus, we treated a mixture of the esters 7a and 7b [60:40] with DMSO/I_2 and, on the other hand, we oxidised a mixture of 4a and 4b [60:40] with *m*-chloroperbenzoic acid. Both reactions were found to occur stereospecifically and gave a mixture of the diastereomeric phosphinates (8), however, with the opposite diastereoisomeric content. Since the oxidation of 4 with peracids occurs undoubtedly with retention at P[7], the reaction of 7 with DMSO/I_2 should involve inversion. This is in accord with our earlier results on oxidation of optically active phosphine sulphides and selenides which are converted into corresponding phosphine oxides with inversion at P when DMSO in the presence of acids or iodine is used as oxidizing agent.[8]

Inversion of configuration at P may be explained by assuming that a thiophosphoryl compound and iodine form in the first instance the phosphonium salt (A) which is then attacked by DMSO by means of its nucleophilic O atom. Two intermediate phosphorane structures (B and C) shown below may account for the inversion at P.



The knowledge of the stereochemistry of the oxidation discussed above enabled us to assign the *S* configuration to the diastereoisomeric ester 7a. Consequently, the ester 4a, which on treatment with sulphur afforded 7a with retention at P, should have the *R* configuration whereas the *S* configuration should be ascribed to its isomer 4b.



R-4a *S*-4b

It is interesting to point out that the same conclusion concerning the chirality at P in the diastereoisomeric esters (7a and 7b) can be drawn from the comparison of the ^{1}H NMR spectra (Fig. 1) of 7a and 7b as well as of 8a and 8b with those of the diastereoisomeric O-menthyl methylphenylphosphinate (6) discussed in detail by Mislow *et al.*[9] Particularly useful in this regard was a region for the isopropyl Me protons which is diagnostic of configuration at P. As in the case of the S_p-diastereoisomer of 6, in the spectrum of 7b there was a nicely separated doublet at δ 0.34 ppm due to one of the diastereotopic Me groups. This upfield doublet was not observed in the spectrum of 7a. Similarly, the doublet at δ 0.34 ppm unencumbered by other signals was also observed in the spectrum of 8b but not in the spectrum of 8a. Thus, it may be concluded that the esters (7a and 8a) are homochiral with the R_p-diasteroisomer of 6 and should have the *S* and *R* configuration at P, respectively.

Nucleophilic substitution at phosphorus in O-menthyl ethylphenylphosphinites (4). After assigning the absolute configuration to the diastereoisomeric esters (4a and 4b) it was of interest to examine the stereochemistry of nucleophilic substitution at trivalent P. In the present study methyllithium and dimethylaminolithium were used as nucleophilic reagents. Schemes 3 and 4 summarise configurational correlations and the results obtained.

Treatment of a mixture of 4a and 4b [60:40] with an excess of methyllithium in ether for 8 hr under reflux followed by an aqueous quench and distillation gave (−)-methylethylphenylphosphine (10), δ_p 32.9 ppm, which was contaminated with a small amount of menthol. Therefore, the phosphine (10) obtained was converted into the corresponding phosphinoxide (9), phosphinesulphide (11) and benzylphosphonium bromide (12). Since the optical purity and absolute configuration of 9[6], 11[10] and 12[11] as well as the stereochemistry of oxidation, sulphurisation and quaternisation of phosphines (retention at P) are known[7] it was possible to establish that the replacement of the OMe group by Me occurs with inversion of configuration at trivalent P atom and with almost complete stereospecificity.

The reaction of a mixture of the diastereoisomeric

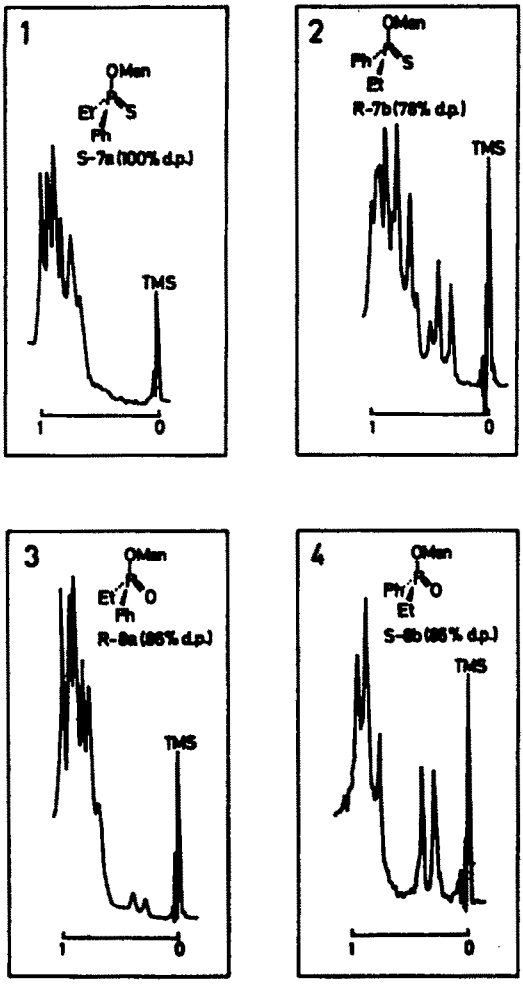
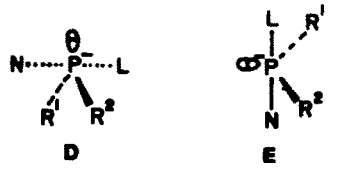


Fig. 1. Pmr spectra (methyl protons region) of diastereoisomeric O-menthyl ethylphenylphosphinothioates (7) and O-menthyl ethylphenylphosphinates (8).

esters (4) [56% of 4a and 44% of 4b] with dimethylaminolithium was found (^{31}P NMR assay) to be complete after 4 hr reflux in ether giving (+) N,N-dimethyl ethylphenylphosphinoamidite (13). It should be pointed out that the latter compound is the first example of the optically active trivalent P amide which may be useful for further transformations. In order to establish optical purity and absolute configuration of 13 two reactions were carried out. Thus, the amide 13 was converted by means of elemental sulphur into (−) N,N-dimethyl ethylphenylphosphinoamidothioate (14) which in turn on treatment with water in the presence of hydrochloric acid gave well-known, optically active (−)-ethylphenylphosphinothioic acid (15)[12] characterised as dicyclohexylammonium salt.† Since sulphur addition to P^{III} compounds proceeds with retention at P and the acid-catalysed hydrolysis of 14, like the acid-catalysed alcoholysis of phosphinate esters,[14] occurs undoubtedly with inversion of configuration at phosphorus it follows that the chirality at P in (+)-13 is *S*. Hence, the replacement of the OMe group by dimethylamino group takes place with inversion of configuration at P and high stereospecificity.

The results on nucleophilic substitution at the optically active trivalent P atom presented above together with the data published so far[4,15] strongly support the general statement that nucleophilic displacement at P^{III} containing two direct C–P bonds and a leaving group like alkoxy, thioalkoxy and aryl occurs with complete inversion of configuration at chiral P. However, the question whether this reaction proceeds according to a classical S_N2–P process involving the transition state D or via addition-elimination mechanism with the transient formation of a valency-expanded anionic intermediate E is still open.



If the latter possibility is true, the intermediate E formed would have a trigonal bipyramidal structure‡ in which a nucleophilic agent (N) and a leaving group L occupy apical positions and two substituents as well as an electron pair lie in equatorial positions. Since this situation is most convenient from the point of view of apicophilicity of substituents in trigonal-bipyramidal phosphoranes it seems likely that such a species would have a large enough barrier for the Berry-type pseudorotation to make such a process slow relative to the product forming step of the reaction. Further studies on this problem are in progress.

EXPERIMENTAL

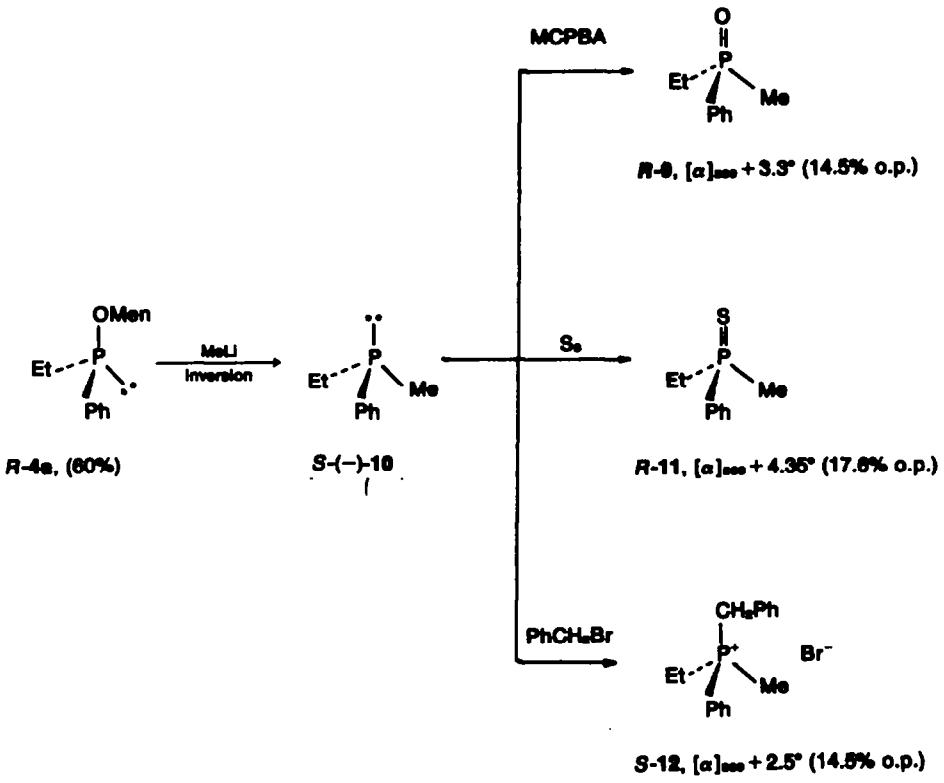
All m.ps and b.ps are uncorrected. Solvents and commercial reagents were distilled and dried by conventional methods before use; diethyl ether was distilled from LAH. Ethylphenylchlorophosphine was obtained by alkylation of phenyldichlorophosphine with $PbEt_4$ according to procedure described by Kharasch.[17] Natural menthol was used without purification from BDH company.

^{1}H NMR spectra were recorded at 60 MHz with R12B Perkin–Elmer spectrometer using TMS as an internal standard. ^{31}P NMR spectra were obtained on a Joel-JNM-FX60 Fourier transform spectrometer at 24.3 H_z with 85% H_3PO_4 as external standard. In this paper the now convention of positive ^{31}P NMR signals to low field from H_3PO_4 is used. Optical activity measurements were made with a Perkin–Elmer 241MC photopolarimeter (sensivity ±0.002°). Column chromatography was done on silica gel Merck 100–200 mesh.

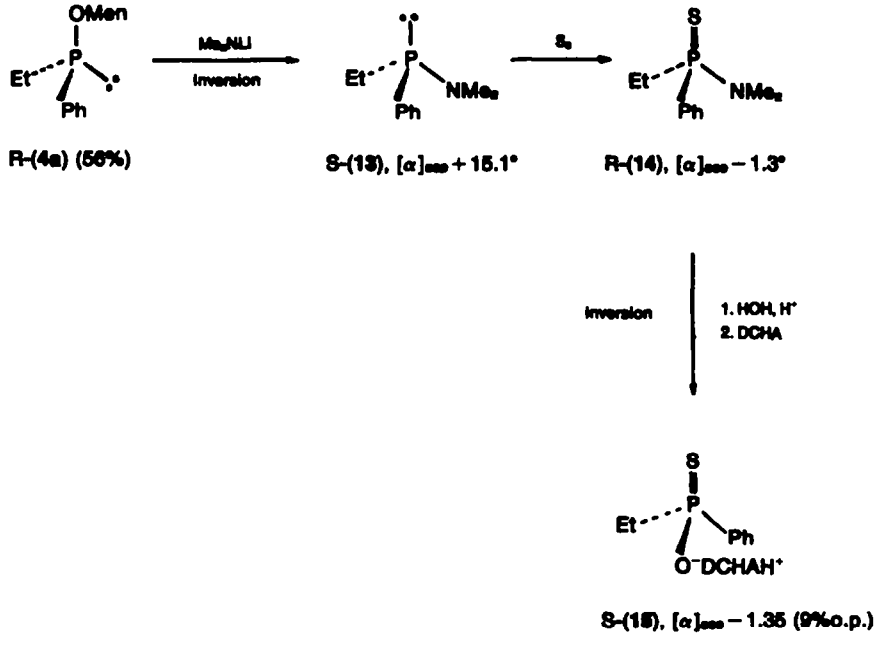
Diastereoisomeric O-menthyl ethylphenylphosphinites (4a and 4b). To a soln of ethylphenylchlorophosphine (3.52 g, 0.0204 mol) in ether (50 ml) a soln of menthol (3.18 g, 0.0204 mol) and N,N-diethyl aniline (3.04 g, 0.0204 mol) in ether (15 ml) was added at −30° under N_2. The mixture was stirred at this temp. for 0.5 hr and then at room temp. for 1 hr. The N,N-diethylaniline hydrochloride was filtered off (under N_2) and after evaporation of ether the crude product 4 (4.5 g, 80%) was obtained. The ratio of diastereoisomers (4a and 4b) was determined by ^{31}P NMR as 60:40; δ_P (benzene) 116.6 ppm and 115.0 ppm. Distillation of the product gave an equimolar mixture of the diastereoisomers (4a and 4b). The ester 4 was sensitive to oxygen and was contaminated with a small amount of the oxidised product 8a and 8b (up 3%). The ratio of the diastereoisomeric esters 4a and 4b obtained from other experiments is summarised in Table 1.

†Optical purity of thioacid (15) was determined by NMR method *via* the diastereoisomeric salts with optically active α-naphthylethylamine.[13]

‡It is worthy of mention that sulphuranes having four substituents and lone electron pair connected with the central sulphur atom adopt also trigonal bypiramidal structure in which electron pair occupies an equatorial position.[16]



Scheme 3.



Scheme 4.

Diastereoisomeric O-*menthyl ethylphenylphosphinothioates* (7a *and* 7b). To a mixture of 4a and 4b [68:32] (5.84 g, 0.02 mol) in ether (30 ml) elemental S (0.0704 g, 0.022 mol) was added under N_2 at room temp. The mixture was stirred 1 hr and the excess of S was filtered off. After evaporation of ether the residue was placed in a refrigerator. The crystalline product was filtered off (5.4 g, 99%). The ratio of diastereoisomers (7a and 7b) was determined by ^{31}P NMR in benzene as 68:40 (δ_p 90.5 ppm and 92.0 ppm) (Found: C, 64.87; H, 8.95; P, 9.64. Calc. for $C_{22}H_{39}OPS$ (324.46): C, 66.65; H, 9.91; p, 9.54%). Crystallization of the mixture 7a and 7b (68:32) from ether or EtOAc (15 ml) gave the pure diastereoisomer 7a (3.2 g), δ_p (benzene) + 90.5 ppm; m.p. 108–110°, $[\alpha]_{546}$ − 45.9° (c, 2.83; benzene). The mother liquor contained the mixture of 7a and 7b in a ratio 17:83.

Diastereoisomeric O-*menthyl ethylphenylphosphinates* (8a *and* 8b)

(A) *Oxidation of diastereoisomeric* O-*menthyl ethylphenylphosphinites* (4) *by MCPBA.* To a soln of (4a) and (4b) 38.5:61.5 (3.22 g, 0.011 mol) in ether (70 ml) a soln of *m*-chloroperbenzoic acid (4.32 g, 0.025 mol) was added at −25° under N_2. The mixture was stirred at this temp for 0.5 hr and then at room temp for 1 hr. After evaporation of ether the residue was treated with $CHCl_3$ (30 ml). The organic soln was washed with 5% HCl, $NaHCO_3$ aq, water, dried over $MgSO_4$ and evaporated to give the crude mixture of 8a and 8b which was purified by column chromatography (eluent–benzene:acetone 6:1). The ratio of 8a and 8b (3 g, 88%) was found to be 38.5:61.5 δ_P (benzene) 41.1 ppm and 42.1 ppm], n_D^{25} 1.5127, $[\alpha]_{589}$ − 39.6 (*c*, 2.51, benzene) (Found: C, 70.14; 9.52; P, 9.88. Calc. for $C_{18}H_{29}O_2P$ (308.40) C, 70.10; H, 9.48; P, 10.04%).

(B) *Oxidation of* O-*menthyl ethylphenylphosphinothionate* (7a) *by DMSO/*I_2. A soln of 7a (3.0 g, 0.0092 mol) and I_2 (1.16 g, 0.0046 mol) in DMSO (23 g) was heated at 80° for 15 hr and after cooling it was poured into water (100 ml). The water phase was extracted with $CHCl_3$ (5 × 20 ml) and organic layer was washed with $Na_2S_2O_3$ aq, water and dried over $MgSO_4$. Solvent was evaporated and the crude product was discoloured with charcoal in benzene (30 ml). Evaporation of benzene and column chromatography gave 8b (2 g, 72%) 98% d.p.; [δ_P ($CHCl_3$) 44.2 ppm], 8a [δ_P ($CHCl_3$) 43.3 ppm], n_D^{25} 1.5900, $[\alpha]_{589}$ − 54.3 (*c*, 2.34, benzene).

Starting from the mixture of 7a and 7b [60:40] (1.3 g, 0.004 mol), I_2 (0.5 g, 0.002 mol) and DMSO (10 g) the mixture of 8a and 8b [41:59] (1.1 g, 90%) was obtained in the same manner as described above; n_D^{25} 1.5130, $[\alpha]_{589}$ − 47.1 (*c*, 4.22, benzene).

(C) *Oxidation of* O-*menthyl ethylphenylphosphinothionate* (7a) *by* H_2O_2. Oxidation of 7a by H_2O_2 in EtOH was performed according to the procedure described by Trippett.[18] Starting from the diastereoisomeric ester 7a (0.5 g, 0.00154 mol), H_2O_2 (1.2 mol, 30%) and EtOH (10 ml) the mixture of 8a and 8b [86.2:13.8] was obtained; 0.4 g, 91%; $[\alpha]_{589}$ − 24.5 (*c*, 2.27, benzene) [δ_P 44.2 ppm and 43.3 ppm ($CDCl_3$)].

(D) *Oxidation of* 7a *by* MCPBA.[18] Oxidation of 7a (1 g, 0.0031 mol) by 60% MCPBA (1 g, 0.0048 mol) in CH_2Cl_2 (60 ml) was carried out at 0° for 2.5 hr. The soln was washed with 5% HCl, $NaHCO_3$ aq, H_2O, dried over $MgSO_4$ and evaporated to give the mixture of 8a and 8b [54:44] (0.9 g); $[\alpha]_{589}$ − 42.5 (*c*, 4.06, benzene), n_D^{25} 1.5109.

(−) *Methylethylphenylphosphine oxide* (9). The phosphine oxide 9 was obtained from 8b (98% d.p. 2g, 0.0065 mol) and MeMgI [prepared from Mg (0.8 g, 0.0325 mol) and MeI (5.2 g, 0.036 mol)] in ether (40 ml) according to procedure described;[6] 0.1 g $[\alpha]_{589}$ − 18.1 (*c*, 2.53, MeOH), δ_P (CD_3OD) 37.5 ppm.

Optically active methylethylphenylphosphine (10) *from diastereoisomeric esters* (4a *and* 4b). To a soln of 4a and 4b [60:40] (7.1 g, 0.0244 mol) in ether (60 ml) MeLi (prepared from 1.4 g, 0.2 mol Li and 14.1 g, 0.1 mol MeI) in ether (40 ml) was added at room temp under N_2. The mixture was refluxed for 8 hr and then EtOAc (10 ml) and water (20 ml) was added at 0°. The water layer was extracted with ether (3 × 15 ml) and the combined organic solns were dried and evaporated to give after distillation 10 (3.2 g; δ_P − 32.9 ppm) contaminated with menthol. For that reason 10 was characterised as corresponding (+) phosphine oxide 9, (+) phosphine sulphide 11 and (+) phosphonium bromide 12.

(+) *Methylethylphenylphosphine oxide* (9). It was obtained from 10 (1.04 g, 0.0069 mol) and *m*-chlorobenzoic acid (2.58 g, 0.015 mol) in ether (15 ml) at −25° under N_2. The product was purified by column chromatography (benzene–acetone 4:1) and distillation to give (+)-9 (1 g, 86%) $[\alpha]_{589}$ + 3.3 (*c*, 5.10, MeOH); δ_P (CD_3OD) 37.5 ppm).

(+) *Methylethylphenylphosphine sulphide* (11). It was obtained from 10 (0.83 g, 0.0055 mol) and elemental S (0.18 g, 0.0056 mol) in ether (15 ml). The excess of S was filtered off from MeOH soln (5 ml) and the crude 11 was chromatographed (benzene) giving (+)-11 (0.9 g, 89%); $[\alpha]_{589}$ + 4.4 (*c*, 2.76, MeOH); m.p. 38–40°; δ_P (CD_3OD) 42.4 ppm.

(+) *Methylphenylbenzylphosphonium bromide* (12). It was synthesized by quaternisation of 10 (0.61 g, 0.004 mol) with benzyl bromide (0.68 g, 0.004 mol) in MeCN (10 ml) according to procedure described[11] to afford (+)-12 (1.2 g, 98%); $[\alpha]_{589}$ + 2.5 (*c*, 2.35, MeOH) m.p. 142–143°, δ_P (MeOH) 28.8 ppm.

(+)-N,N-*Dimethyl ethylphenylphosphinoamidite* (13) *and* (−)-N,N-*dimethyl ethylphenylphosphinoamidothionate* (14). To a soln of Me_2NLi (prepared from 0.13 mol BuLi and 7.2 g Me_2NH) in ether (130 ml) was added a soln of a mixture of 4a and 4b [56:44] (7.5 g, 0.026 mol) in ether (20 ml) at −20° under N_2. The mixture was stirred at room temp for 1 hr and then was refluxed for 4 hr. Ether was evaporated and the residue was treated with petroleum ether (30 ml). The soln was filtered under N_2. After evaporation of the solvent the product was distilled to give (+)-13 (2.1 g), $[\alpha]_{589}$ + 15.1 (*c*, 4.85, benzene); δ_P (benzene) 61.5 ppm. The product was contaminated with an admixture of menthol and therefore it was converted into 14.

To a soln of (+)-13 (0.91 g, 0.005 mol) in benzene (15 ml) elemental S was added (0.25 g, 0.008 mol) at room temp under N_2. After evaporation of benzene, MeOH (5 ml) was added, the excess of S filtered off and the residue purified by column chromatography (benzene). Final distillation gave (−)-14 (0.7 g, 70%), $[\alpha]_{589}$ − 1.3 (*c*, 3.72, benzene), δ_P (benzene) 79.6 ppm. The product 14 was also pure by glc (Found: C, 56.49; H, 7.81; P, 13.53; S, 14.40. Calc. for $C_{10}H_{16}NPS$ (213.28), C, 56.32; H, 7.56; P, 14.52; S, 15.03%).

Dicyclohexylammonium salt of (−)-*ethylphenylphosphinothioic acid* (15). A soln of (−)-14 (0.6 g, 0.0028 mol) and 12% HCl (15 ml) was heated for 5 hr at 60–65°. After cooling the soln to room temp the product was extracted with $CHCl_3$ (5 × 15 ml), dried over $MgSO_4$ and evaporated to give the crude (−)-15. It was characterised as dicyclohexylammonium salt; (0.42 g, 90%), $[\alpha]_{589}$ − 1.35 (*c*, 1.63, MeOH) m.p. 144–147°, δ_P (MeOH) 66.0 ppm.

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