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A NEW ENANTIOSELECTIVE ASYMMETRIC SYNTHESIS OF TRI-CO-ORDINATE PHOSPHORUS COMPOUNDS FROM DI-CO-ORDINATE λ^3 -ARYL(ALKYL)IMINOPHOSPHINES

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SHORT COMMUNICATION

A new enantioselective asymmetric synthesis of tri-co-ordinate phosphorus compounds from di-co-ordinate λ^3 -aryl(alkyl)iminophosphines

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and

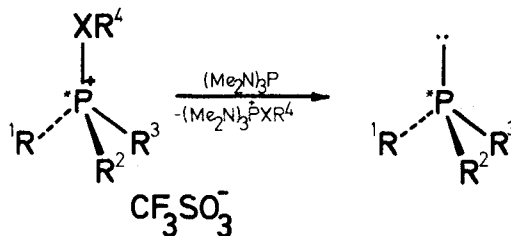
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The reaction of di-co-ordinate λ^3 -aryl(alkyl)iminophosphines (1) with achiral alcohols in the presence of optically active tertiary amines has been found to proceed in an asymmetric way affording optically active O-alkyl amidophosphonites (2). N-(2,4,6-Tris-*t*-butylphenyl)amido-O-methyl-phenyl-phosphonite (2a) was obtained in this way with 55% ee and the absolute configuration (S) was chemically linked with (+)-(R)-O-methyl *t*-butanephosphonothioic acid.

During the past few years, much effort has been devoted to the synthesis and transformations of optically active tri-co-ordinate phosphorus compounds, especially those containing the phosphorus-oxygen, phosphorus-sulphur and phosphorus-nitrogen bond.^{1,2} A general, highly stereoselective synthesis of such compounds developed in our laboratory³ involves the reaction of optically active alkylthio(alkylseleno)phosphonium salts with tris-(dimethylamino)-phosphine shown below.



X=S, Se

• - denotes optically active centre

In this paper we wish to report a new approach to optically active tri-coordinate phosphorus compounds starting from λ^3 -aryl(alkyl)iminophosphines **1**. These thermally stable, di-co-ordinate phosphorus compounds have recently been synthesized in Kiev⁴ and found to react with some nucleophilic reagents (alcohols, amines) to give the corresponding addition products containing the tri-co-ordinate phosphorus atom.⁵ Now, we found that the reaction of equimolar amounts of iminophosphines **1**, achiral alcohols and optically active tertiary amines carried out in benzene or ether solution at temperatures from -78° to $+25^\circ\text{C}$ occurs in an asymmetric way and results in the formation of the optically active amidoesters **2**. The latter on account of their sensitivity to hydrolysis and oxidation were converted by means of elemental sulphur into the corresponding thiono-derivatives **3** which were purified by column chromatography and characterized by elemental analysis and ^1H and ^{31}P n.m.r. spectra. The results of these reactions are summarized in Table I.

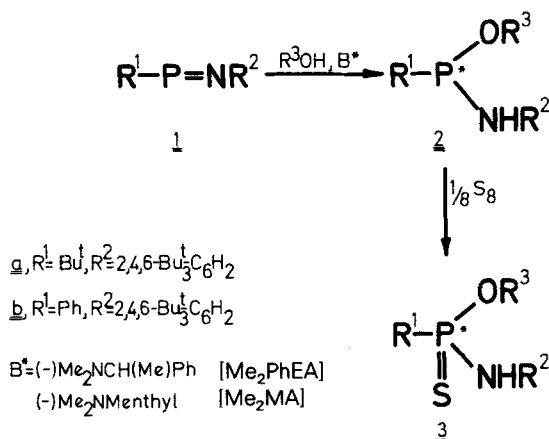


TABLE I

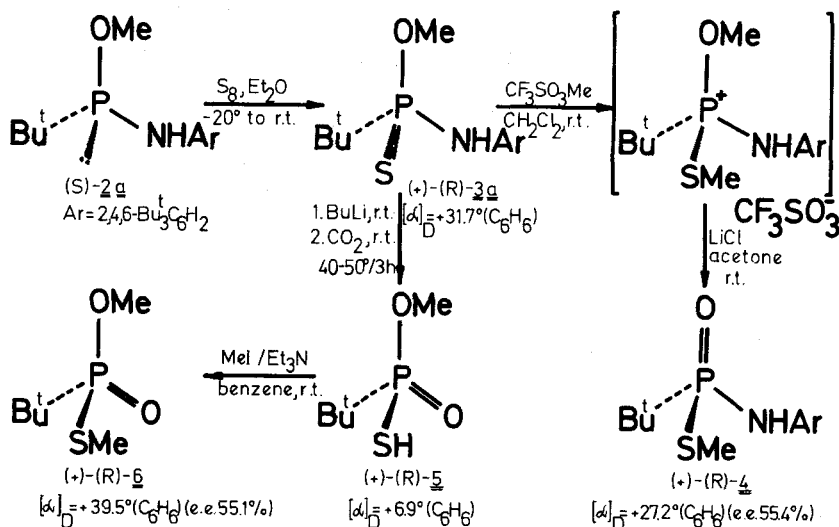
Asymmetric synthesis of N-aryl(alkyl)amido O-alkyl phosphonites **2**, $\text{R}^1\text{P}(\text{OR}^3)\text{NHR}^2$, and their conversion into N-aryl(alkyl)amido O-alkyl phosphonothionates **3**, $\text{R}^1\text{P}(\text{S})(\text{OR}^3)\text{NHR}^2$, [$\text{R}^2 = 2,4,6\text{-Bu}_3\text{C}_6\text{H}_2$]

| Iminophosphine 1 | | Chiral amine | Reaction time | Reaction temp. ($^\circ\text{C}$) | Amidoester 2 ^a | | Amidothioester 3 ^a | |
|-------------------------|-----------------|----------------------|---------------|-------------------------------------|----------------------------------|-----------------|--------------------------------------|--|
| No | R ¹ | | | | No | R ³ | No | $[\alpha]_{589}(\text{C}_6\text{H}_6)$ ($^\circ$) |
| 1a | Bu ^t | Me ₂ PhEA | 0.5 h | +25 | 2a | Me | 3a | -4.4 |
| 1a | Bu ^t | Me ₂ MA | 4.0 h | 0 | 2a | Me | 3a | +20.0 |
| 1a | Bu ^t | Me ₂ MA | 3.0 h | -5 | 2a | Me | 3a | +31.7 |
| 1a | Bu ^t | Me ₂ MA | 31.0 h | -76 | 2a | Me | 3a | +30.8 |
| 1a | Bu ^t | Me ₂ PhEA | 24.0 h | +25 | 2a' | Pr ⁱ | 3a' | +0.5 |
| 1a | Bu ^t | Me ₂ MA | 11 d | +25 | 2a' | Pr ⁱ | 3a' | +0.7 |
| 1b | Ph | Me ₂ PhEA | 5 min | +25 | 2b | Me | 3b | -4.6 |
| 1b | Ph | Me ₂ MA | 20 min | 0 | 2b | Me | 3b | +7.4 |
| 1b | Ph | Me ₂ PEA | 3.0 h | 0 | 2b' | Pr ⁱ | 3b' | -4.0 |
| 1b | Ph | Me ₂ MA | 3.0 h | 0 | 2b' | Pr ⁱ | 3b' | -0.2 |

^a $\delta_{31\text{P}}[\text{ppm}, \text{C}_6\text{H}_6]$ for the esters **2** and **3**: **2a**, 145.7; **3a**, 97.8; **2a'**, 140.7; **3a'**, 95.9; **2b**, 122.4; **3b**, 78.0; **2b'**, 120.3; **3b'**, 74.2.

In order to determine the extent of asymmetric induction in the reaction investigated and to establish the absolute configuration of amidophosphonites **2** it was necessary to perform some additional reactions of amidothiophosphonates **3**. For example, the enantiomeric excess value in (+)-**3a**, $[\alpha]_D +31.7^\circ$, was determined very easily by combination of the chemical and spectroscopic methods. Thus, the thiophosphonate (+)-**3a**, $[\alpha]_D +31.7^\circ$, was transformed into its thioisomer (+)-**4a**, $[\alpha]_D +27.2^\circ$, by treatment at first with methyl triflate and then with lithium chloride.⁶ The ¹H-n.m.r. spectrum of this ester measured in carbon tetrachloride solution containing (+)-*t*-butylphenylphosphinothioic acid⁷ revealed the presence of two diastereoisomeric solvates in a 77.7:22.3 ratio which corresponds to 55.4% ee. Since the isomerization of (+)-**3a** into (+)-**4a** takes place without bond breaking around the chiral phosphorus atom, the same enantiomeric purity should be ascribed to the ester (+)-**3a** and also to **2a** if we assume that the sulphur addition to the latter proceeds with full retention of configuration.⁸

The chirality at phosphorus in (+)-**3a** was established chemically by means of its conversion into (+)-*O*-methyl *t*-butanephosphonothioic acid **5**⁹ utilizing the Wadsworth–Emmons reaction. Since the Wadsworth–Emmons reaction has been shown¹⁰ to occur with retention of configuration at phosphorus and the chirality of the thioacid (+)-**5** is (R),¹¹ the chirality at phosphorus in (+)-**3a** should be (R). Consequently, the chirality at phosphorus in **2a** obtained in the asymmetric reaction should be (S). It is interesting to add that methylation of the thioacid (+)-(R)-**5**, $[\alpha]_D +6.9^\circ$, with methyl iodide gave the corresponding thiophosphonate (+)-(R)-**6**, $[\alpha]_D +39.5^\circ$. The ee value of this ester determined by the ¹H-n.m.r. method via the diastereoisomeric solvates with (+)-*t*-butylphenylphosphinothioic acid was found to be 55.1%. The latter value is in excellent agreement with that found for the ester (+)-**4**. The chemical correlation discussed above is shown in Scheme 1.



SCHEME 1 Assignment of the absolute configuration (and optical purity) of **2a**.

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