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Preliminary communication

STEREOSELECTIVE DESELENISATION OF t-BUTYLPHENYLPHOSPHINOSELENOIC ACIDS. STEREOCHEMICAL RELATIONSHIP BETWEEN t-BUTYLPHENYLPHOSPHINOSELENOIC ACIDS AND THEIR SULPHUR ANALOGUES

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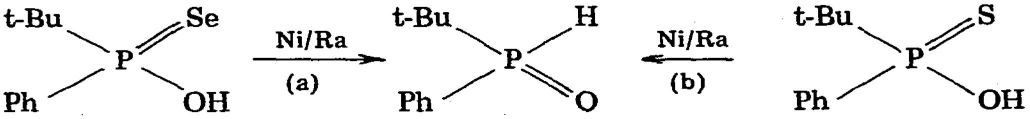
Summary

Deselenisation of the optically active monoselenoacids lead to disubstituted phosphine oxides with high optical yield and the reaction provides a means of correlating chiral phosphorus monoselenoacids with their sulphur analogues.

We recently reported the resolution of monoselenoacid of phosphorus [1]. Treatment of optically active t-butylphenylphosphinoselenoic acids (I) with Raney nickel (reflux in ethanol solution under argon, for 10 h) gave optically active t-butylphenylphoshine oxides (II) (60 MHz, ^{1}H NMR ($CDCl_3$), δ (ppm) 1.15 (9H, d, J(P—C—CH_3) 16.9 Hz); 8.1 (1H, d, J(P—H) 456 Hz); 7.6 (5H, m) IR (KBr): ν(P=O) 1170 and 1270 ν(P—H) 2320-2375).



(I)	(II)	(III)
($[\alpha]_D^{20}$ +24.1°, c (g/100 ml) 1, methanol m.p. 97 °C)	(a: $[\alpha]_D^{20}$ —28.8°, c (g/100 ml) 2, benzene, m.p. 72-74 °C.) (b: $[\alpha]_D^{20}$ —27.6°, c (g/100 ml) 2, benzene, m.p. 70-74 °C)	($[\alpha]_D^{20}$ +21.5°, c (g/100 ml) 1.5, methanol, m.p. 96 °C)

The optical purity of the phosphine oxide (II) is close to that of the oxide prepared by desulphurisation of the optically active t-butylphenylphosphinothioic acid (III) [2]. It is most likely that both deselenisation and desulphurisation reactions follow the same stereochemical course. Consequently

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it can be deduced that the t-butylphenylphosphinoselenoic acid (I) and t-butylphenylphosphinothioic acid (III) of the same rotation sign have the same absolute configuration. Further conformation of this relationship can be found in the addition of elemental selenium and elemental sulphur to the phosphine oxide (II) since the addition of sulphur and selenium to II is most likely to proceed with retention of configuration at the phosphorus atom [2].

$$\mathrm{I} \xleftarrow[\text{(2) HCl}]{\text{(1) Se}_x\ +\ \text{NEt}_3} \mathrm{II} \xrightarrow[\text{(2) HCl}]{\text{(1) S}_x\ +\ \text{NEt}_3} \mathrm{III}$$

($[\alpha]_D^{20}$ −26.2°, *c* (g/100 ml) 1.5, methanol, m.p. 95 °C)	($[\alpha]_D^{20}$ +27.9°, c (g/100 ml) 2, benzene, m.p. 72-74 °C)	($[\alpha]_D^{20}$ −19.5° *c* (g/100 ml) 1.5, methanol, m.p. 93-94 °C)

Comparison of the specific rotation of the acids I and III used in the deselenisation and desulphurisation procedures leading to II with those obtained by addition of the corresponding elements to the oxide II indicates a high stereoselectivity in all these reactions.

Phosphine oxide II can be readily converted by the Michaelis—Becker reaction into t-butylmethylphenylphosphine oxide IV without change of configuration at the phosphorus atom (60 MHz, ^{1}H NMR ($CDCl_3$) δ (ppm) 1.05 (9H, d, *J*(P—C—CH_3) 14.7 Hz); 1.5 (3H, d, *J*(P—C—H) 12 Hz); 7.45 (5H, m)).

$$\mathrm{II} \xrightarrow[\text{benzene}]{\text{NaH}} \text{t-BuPhPONa} \xrightarrow[\text{benzene}]{CH_3I} \text{t-BuPhCH}_3\text{P(O)}$$

(IV)

($[\alpha]_D^{20}$ −27.6°, *c* (g/100 ml) 2, benzene)	($[\alpha]_D^{20}$ −10.2° *c* (g/100 ml) 2, benzene)

The absolute configuration of IV is known [3], it can therefore be concluded that monoselenoacids (I) and monothioacids (III) of +-rotation value have (*R*) configurations.

The structures of all the compounds described above were confirmed by elemental analysis and mass spectra.

References

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