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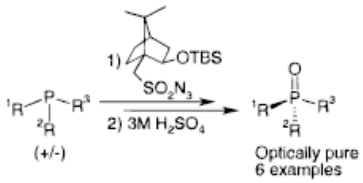
Citation:

A Novel Resolution Procedure for the Preparation of P-Stereogenic Phosphine Oxides
Neil G. Andersen, Philip D. Ramsden, Daqing Che, Masood Parvez, and Brian A. Keay
pp 2009 – 2011.

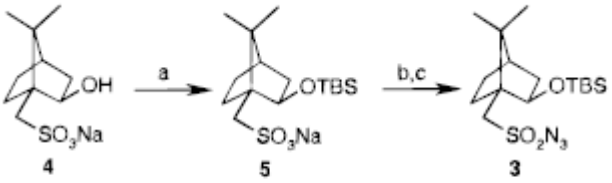
Abstract:



A new general route for preparing enantiomerically pure P-stereogenic phosphine oxides has been developed by exploiting the Staudinger reaction between racemic tertiary phosphines and an enantiomerically pure organoazide. The resulting phosphinimines are easily resolved by either crystallization or flash chromatography and serve as synthetic intermediates toward enantiomerically pure phosphine oxides.

Schemes:

Scheme 1. Synthesis of the Resolving Agent[9] [a]



[a] Reagents and conditions: (a) TBSCl, Et_3N, DMF, rt, 3 h; (b) $SOCl_2$, C_6H_6, DMF; reflux 12 h; (c) NaN_3, DMA, H_2O, 60 °C 12 h, 57% isolated yield from 4.

Figures:

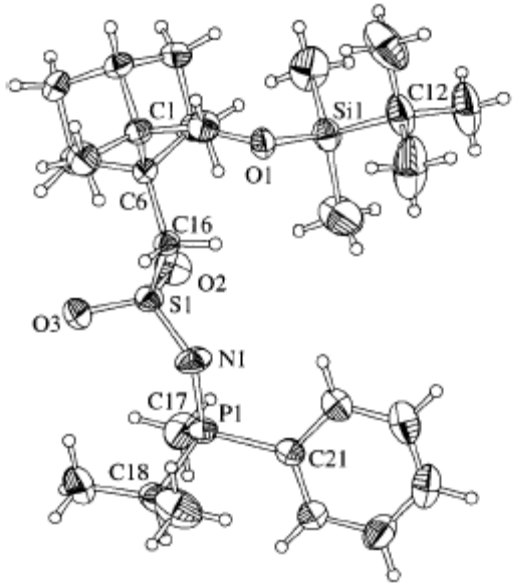
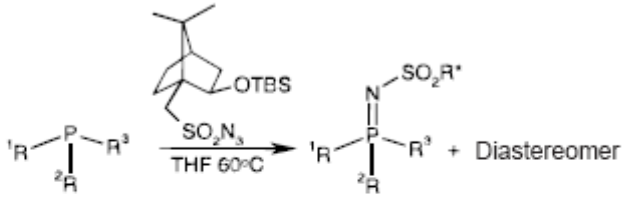


Figure 1. ORTEP drawing of phosphinimine **6c**[18] drawn with 30% probability ellipsoids, except for the hydrogen atoms which are represented as spheres of arbitrary size.

Tables:

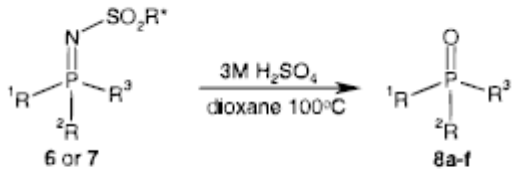
Table 1. Treatment of Racemic Phosphines with Azide 3[14]



1a-f **6a-f** **7a-f**

entry	R^1	R^2	R^3	yield (%)
1a	Ph	Me	C_6H_{11}	94
1b	Ph	Me	C_5H_9	90
1c	Ph	Me	$CH(CH_3)_2$	87
1d	Ph	Me	1-naphthyl	94
1e	Ph	Me	9-phenanthryl	89
1f	Ph	1-naphthyl	*p*-PhC_6H_4	91

Table 2. Hydrolysis of Isomerically Pure Phosphinimines



6 or 7 → 8a-f

SM	R^1	R^2	R^3	yield (%)
6a	Ph	Me	C_6H_{11}	93
7b	Ph	Me	C_5H_9	93
6c	Ph	Me	$CH(CH_3)_2$	94
6d	Ph	Me	1-naphthyl	96
6e	Ph	Me	9-phenanthryl	>99
7f	Ph	1-naphthyl	*p*-PhC_6H_4	93

Table 3. Assignment of Phosphinimine Absolute Configuration from Hydrolysis Product Optical Rotation Data

			configuration	
SM	yield (%)	product α^{20}_D (*c*, solvent)	product **8**	SM
6a	93	+19.2 (0.93, MeOH)[21]	*R*p	*S*p
7b	93	+33.3 (1.62, MeOH)		
6c	94	−22.6 (1.00, MeOH)[22]	*S*p	*R*p
6d	96	+19.8 (2.92, MeOH)[23]	*S*p	*R*p
6e	>99	+71.4 (1.14, MeOH)[24]		
7f	93	+26.9 (0.62,$CHCl_3$)[25]	*R*p	*S*p

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