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Citation:

A Simple Resolution Procedure Using the Staudinger Reaction for the Preparation of *P*-Stereoogenic Phosphine Oxides

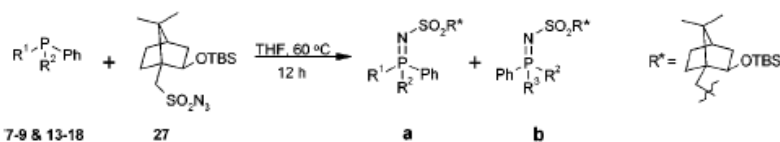
Neil G. Andersen, Philip D. Ramsden, Daqing Che, Masood Parvez, and Brian A. Keay
pp 7478 – 7486.

Abstract:

The resolution of a variety of (\pm)-*P*-stereogenic phosphines is achieved by exploiting the Staudinger reaction of a (\pm)-phosphine with enantiopure (1*S*,2*R*)-*O*-(*tert*-butyldimethylsilyl)isobornyl-10-sulfonyl azide. The resulting mixtures of diastereomeric phosphinimines are generally separable by fractional crystallization or flash chromatography. Subsequent acid-catalyzed hydrolysis provides the corresponding optically pure phosphine oxides in high yields.

Tables:

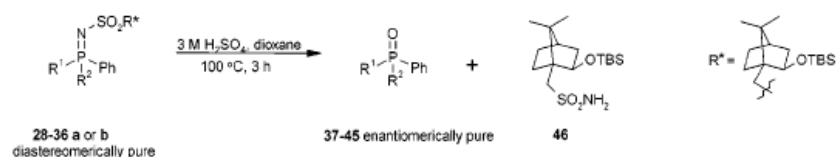
Table 1. Resolution of *P*-Stereoogenic Phosphines with Sulfonyl Azide 27



entry	SM	R ¹	R ²	products ^a	separation method	yield (%) ^b
1	7	Me	C ₆ H ₁₁	28a and 28b	crystallization	94
2	8	Me	C ₅ H ₉	29a and 29b	crystallization	90
3	9	Me	CH(CH ₃) ₂	30a and 30b	crystallization ^c	87
4	13	Me	1-Np	31a and 31b	chromatography	94
5	14	Me	2-Me-1-Np	32a and 32b	chromatography	91
6	15	Me	2-MeO-1-Np	33a and 33b	chromatography	95
7	16	Me	2-Np	34a and 34b	crystallization	87
8	17	Me	9-phenanthryl	35a and 35b	chromatography	89
9	18	1-Np	<i>β</i> -PhC ₆ H ₄	36a and 36b	chromatography	89

^a Diastereomer to elute first or crystallize first designated "a". ^b Combined isolated yield of both diastereomers. ^c Not fully separated.

Table 2. Hydrolysis of Isomerically Pure Phosphinimines

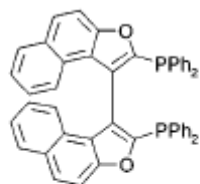


SM	R ¹	R ²	product	expt α_{D}^{20} : [c] (g/100 mL) ^a		lit. α_{D}^{20}	yield (%) ^{b,c}	SM config
1	28a	Me	C ₆ H ₁₁	37	+19.2; [0.93]	+19.0 ²⁸	93 (<i>R</i>)	<i>S</i>
2	29b	Me	C ₅ H ₉	38	+33.3; [1.62]	--	93	--
3	30a	Me	CH(CH ₂) ₂	39	-22.6; [1.00]	-21.2 ³⁰	94 (<i>S</i>)	<i>R</i>
4	31a	Me	1-Np	40	+19.8; [2.92]	+18.6 ³¹	96 (<i>S</i>)	<i>R</i>
5	32b	Me	2-Me-1-Np	41	-73.6; [1.50]	--	94	--
6	33a	Me	2-MeO-1-Np	42	+128.0; [1.58]	+128.0 ¹⁹	91 (<i>S</i>)	<i>R</i>
7	34a	Me	2-Np	43	-12.0; [0.90]	-12.0 ²⁸	96 (<i>S</i>)	<i>R</i>
8	35a	Me	9-phenanthryl	44	+71.4; [1.14]	--	99	--
9	36b	1-Np	<i>p</i> -PhC ₆ H ₄	45	+26.9; [0.62] ^d	+27.0 ^{d,22}	93 (<i>R</i>)	<i>S</i>

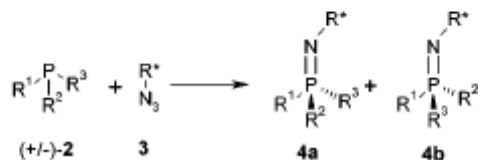
^a Rotation in methanol except as noted. ^b Isolated yields. ^c Phosphorus configuration assigned according to literature correlation. ^d Rotation in CHCl₃.

Schemes:

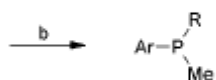
Scheme 1



(+/-)-BINAPFu 1

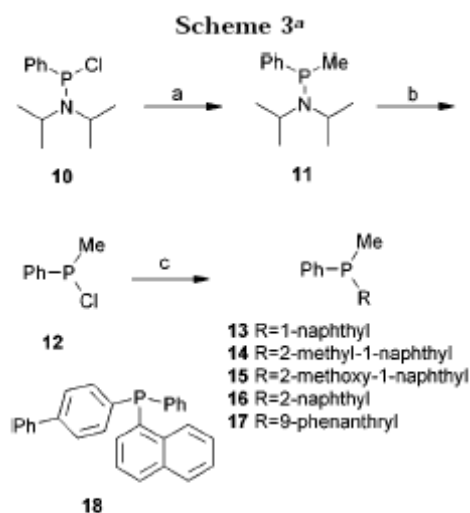


Scheme 2^a

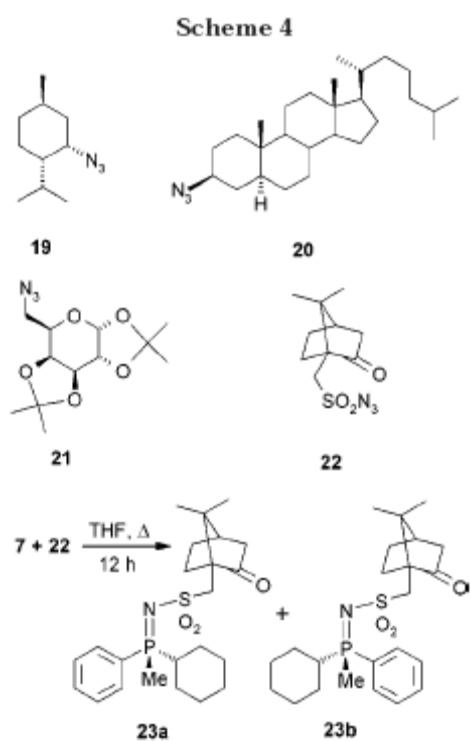


7 R=cyclohexyl
8 R=cyclopentyl
9 R=isopropyl

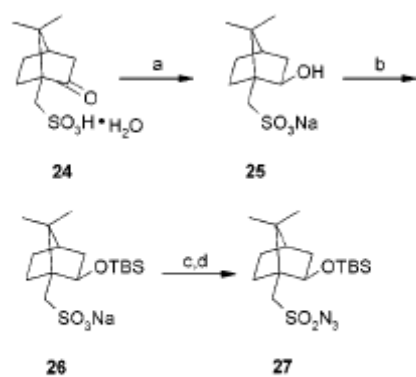
^a Conditions: (a) 2 equiv of MeI, CHCl₃, rt, 24 h. (b) 5 equiv of LiAlH₄, Et₂O, reflux, 6 h.



^a Conditions: (a) 1.0 equiv of MeMgBr, Et₂O, -40 °C, 1 h, 85%.
 (b) 2.2 equiv of HCl (1.0 M solution in Et₂O), 0 °C, 1 h. (c) 1.2 equiv of RMgBr, Et₂O, -40 °C, 3 h, 32–67% (two steps).

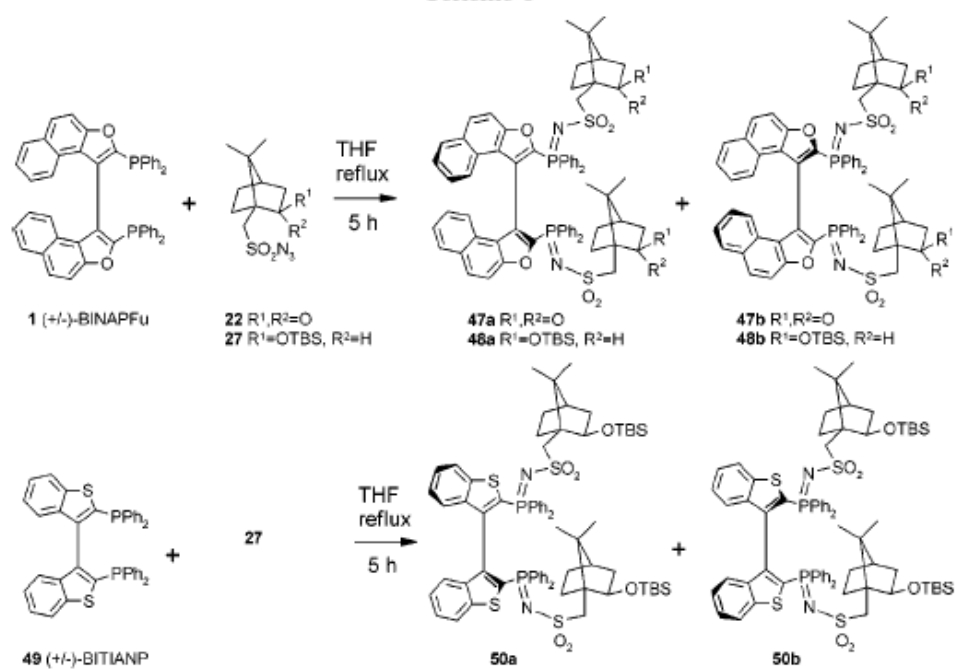


Scheme 5^a

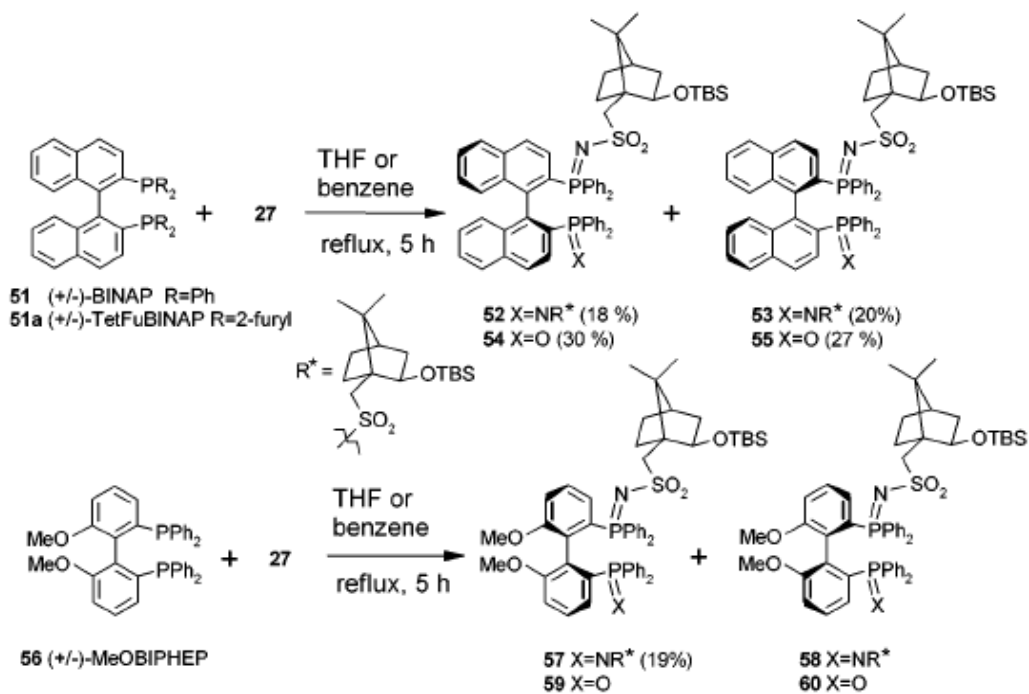


^a Conditions: 2.4 equiv NaBH₄, H₂O, rt, 1 h, 95%. (b) 3.3 equiv TBSCl, Et₃N, DMF, rt, 3 h. (c) 6.0 equiv SOCl₂, C₆H₆, DMF, reflux, 12 h. (d) 3.2 equiv NaN₃, DMA, H₂O, 60 °C, 12 h, 57% (3 steps).

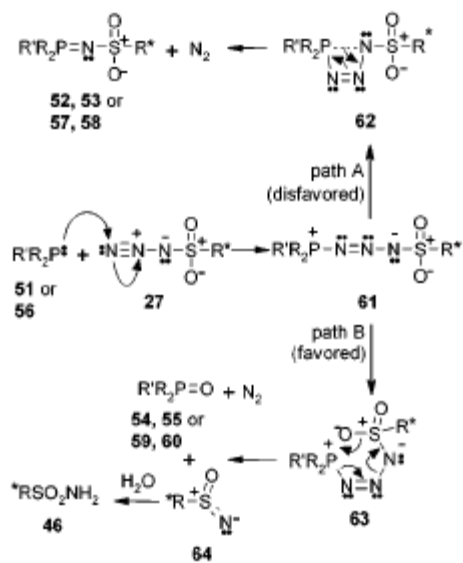
Scheme 6



Scheme 7



Scheme 8

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