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Organic Synthesis with Sulfones n°XXIX

Stereospecific hydrogenolysis of vinylic sulfones with grignards and transition metal catalysts (1).

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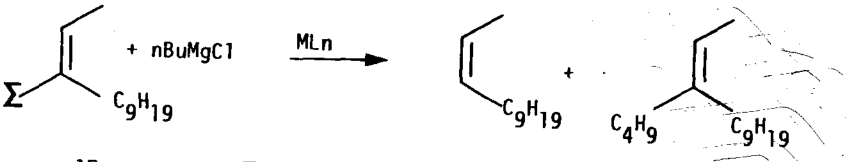
Summary : *Hydrogenolysis of various vinylic sulfones to the corresponding olefins can be carried out by alkyl Grignard reagents with nickel or palladium catalysts. Yields are good to excellent. Retention of configuration is observed. The influence of ligands is discussed.*

A convenient synthesis of E or Z vinyl sulfones has recently been described (2). Substitution with Grignard reagents can be carried out stereospecifically with transition metal catalysts thus providing a stereoselective synthesis of trisubstituted olefins (3). In addition to the iron catalysed substitution by the n-alkyl magnesium halides (63% yield, 97% stereochemical purity), a small amount of hydrogenolysis of the vinylic sulfones had been observed. Isopropyl magnesium bromide, on the other hand, led to a large proportion of hydrogenolysis (50% yield ; 96% stereochemical purity).

Sulfone 1E, (E/Z=99/1) was used to try and find preparatively useful reaction conditions. With nickel and palladium catalysts, the main reaction was hydrogenolysis. In Table I are collected our results with nickel catalysts.



1E Σ = $PhSO_2$ 2 3

. Hydrocarbon 2 was obtained in 48 to 64% yields with an average stereochemistry of 97.5Z/2.5E).

Some (15 - 30%) of the starting sulfone (1E) was recovered unchanged.

. An increase of the n-BuMgCl used (run 8) did not improve significantly the yield of 2.

. The coupling product 3 was formed in very small yields.

Table I : Reaction of sulfone 1E (1mmol) and n-BuMgCl (1.8 mmol) with nickel catalysts (NiLn + yL')(0.01 mmol) in THF (5ml) 24 hrs, r.t., under nitrogen atmosphere.

	NiLn	L'	y	2 (yield)$^{a)}$	(E/Z)	3 (yield) $^{a)}$
1	$Ni(acac)_2$	-	-	64	(2.5/97.5)	4
				$70^{b)}$	(2.5/97.5)	-
				$55^{c)}$	(2.5/97.5)	-
2	$NiCl_2(Ph_3)_2$	-	-	58	(2.5/97.5)	3
3	$NiCl_2$	dppp	1	53	(2.7/97.3)	5
4	$Ni(acac)_2$	$P(nBu)_3$	2	60	(2.5/97.5)	-
5	$Ni(acac)_2$	$P(iPr)_3$	2	48	(2/98)	6
6	$Ni(acac)_2$	DABCO	2	60	(2.5/97.5)	2
7	$Ni(acac)_2$	NEt_3	2	56	(3/97)	3
8	$Ni(acac)_2^{d)}$	-	-	66	(2.5/97.5)	-

DABCO = diazabicyclooctane, dppp : bis(diphenylphosphino)propane .

a) determined by glc. b) $Ni(acac)_2$ 0.05 mmol instead of 0.01 mmol. c) i-PrMgBr instead of n-BuMgCl. d) 4 mmol of n-BuMgCl instead of 1.8 mmol.

Sulfone 1E was next treated with $Pd(acac)_2$ and a few organomagnesium reagents (runs 9-12), and other palladium catalysts with n-BuMgCl (runs 12-19).

Runs 9-12, gave similar results (yields 63-70%) mean stereochemistry (98.5Z/1.5E). Only with n-BuMgBr was the coupling product 3 formed in noticeable amounts (run 11).

In runs 12-19 the ligands strongly influence the yields of 2 and 3 ; the hydrogenolysis product 2 however is always formed with very high retention of configuration (> 98%). Inhibition of the hydrogenolysis occurs with bidentate ligands (run 15) and with aryl phosphine ligands in excess (runs 13-14).

Aryl phosphines seem to inhibit somewhat the hydrogenolysis reaction (runs 13, 14, 15). Tri-n-butylphosphine (run 16) on the other hand led to the best yield. With tri-isopropylphosphine (run 17) a sizeable amount of the coupling product 3 was formed. Triethylamine was found to have no influence (run 19). DABCO led to a slightly higher yield (run 18) (4).

Palladium catalysis appears superior to nickel catalysis in that the stereoselectivity is higher. The yields are also higher as they can be raised by suitable ligands.

Table II : Reactions of sulfone 1E (1mmol) and alkyl magnesium reagents (RMgX)(1.8 mmol) with palladium catalysts (PdLn + yL')(0.01 mmol) in THF (5ml) 24 hrs, r.t. under nitrogen atmosphere.

	R	X	PdLn	L'	y	2 (Yield) a)	(E/Z)	3 (yield) a)
9	iPr	Br	$Pd(acac)_2$	-	-	63	(1.5/98.5)	-
10	iPr	Cl	$Pd(acac)_2$	-	-	67	(1.5/98.5)	-
11	nBu	Br	$Pd(acac)_2$	-	-	60	(2.5.97.5)	9
12	nBu	Cl	$Pd(acac)_2$	-	-	70	(1.5/98.5)	3
13	nBu	Cl	$PdCl_2(PPh_3)_2$	-	-	41	(1.5/98.5)	5
14	nBu	Cl	$PdCl_2(PPh_3)_2$	PPh_3	2	20	-	2
15	nBu	Cl	$PdCl_2$dppp	-	-	21	(2/98)	-
16	nBu	Cl	$Pd(acac)_2$	$P(nBu)_3$	2	83	(1.5/98.5)	5
17	nBu	Cl	$Pd(acac)_2$	$P(iPr)_3$	2	30	(1.5/98.5)	20
18	nBu	Cl	$Pd(acac)_2$	DABCO	2	75	(1.5/98.5)	4
19	nBu	Cl	$Pd(acac)_2$	NEt_3	2	70	(1.5/98.5)	6

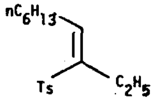
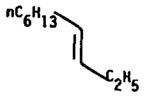
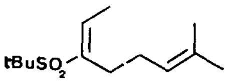
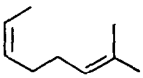
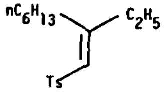
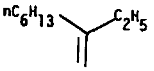
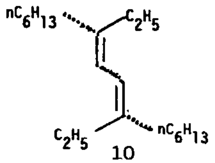
a) determined by glc.

In order to examine the scope of the reaction we synthesized sulfone 4E, 5Z and 6Z according to known procedures (5) and allowed them to react with nBuMgCl and various palladium catalysts (Table III).

For 4Z and 5E hydrogenolysis occurred with good yields and very high retention of configuration. The hydrogenolysis of α,β-disubstituted vinylic sulfones by palladium salts and organomagnesium reagents can be said to be stereospecific.

With the β,β-disubstituted vinylic sulfone 6, in addition to the hydrogenolysis product, a fair amount of the dimers 10 was formed (6).

Table III : Reaction of sulfones 4Z, 5E, 6 with nBuMgCl (1.8 equivalent) and Pd(acac)$_2$ and cocatalysts (2L')(0,01 equivalent) in THF, r.t. under nitrogen atmosphere.

	Starting Sulfone (Stereochemistry)	L'	Hydrocarbon (yield) $^{a)}$ (Stereochemistry)			
20	 4Z (85Z/15E)	P(nBu)$_3$	 7	65% (15Z/85E)		
21	 5E (0Z/100E)	DABCO	 8	70% (99.5Z/0.5E)		
22	 6	-	 9	20%	 10	30%

a) (isolated yield).

This reaction supplements the dithionite method (7) which requires a reaction temperature above 50°C, to give a stereospecific access to disubstituted olefins from vinylic sulfones with good yields and very high stereochemical purity.

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(5) a) 4E according to (2),
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