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Sulfone Directed Rhodium Catalysed Hydroboration: Regiochemistry in Acyclic System

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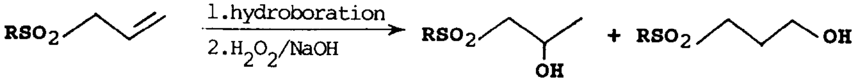
Abstract: Rhodium catalysed hydroboration of allyl sulfones gave rise to Markownikoff product with high regioselectivity.

Hydroboration is one of the most useful reactions in organic synthesis[1]. Since the original findings of Mannig and Noth[2], the metal catalysed variant added another dimention to the hydroboration reaction, and much attention has been focused on the exploitation of its use in organic synthesis[3,4]. Because of the mechanistic dichotomy between two types of reaction[5], the chemo-[2], stereo-[6,7], or regio-selectivities[4,7,8] of the transition metal catalysed hydroboration of certain structural entities are complementary to the conventional hydroboration. Thus, the Rh catalysed hydroboration of styrene gave secondary alcohol by Markownikoff selectivity[7,8], complementary to the conventional hydroboration, which produced primary alcohol by using 9-BBN[1]. To date, there was a few studies about regiochemistry of metal catalysed hydroboration of acyclic system[4,7,8], and Markownikoff selectivities have been found only for alkenes in which aromatic groups are attached directly to the double bond[9]. Evans[4] has successfully controlled the regiochemistry of catalysed hydroboration of acyclic systems by using directing groups, but the regioselectivity for terminal alkene was only 1.2:1. Now we would like to report the Rh catalysed hydroboration of allylic compounds directed by the sulfone group with high regioselectivity at 2-position of a terminal double bond.

The allyl sulfones[10] reacted with catecholborane (CB) in the presence of Wilkinson's catalyst to produce the secondary alcohols (**2**) with small amount of primary alcohols (**3**) after oxidation of hydroborated product (eq. 1). The results were shoun in Table 1.



1 **2** **3**

(eq. 1)

Table 1. comparison of the catalysed and the uncatalysed hydroboration of allyl sulfones

Entry	R	catalysed[a] yield %[c]	catalysed[a] ratio[d] (**2**:**3**)	uncatalysed[b] yield %[c]	uncatalysed[b] ratio[d] (**2**:**3**)
1	Ph	83	87:13	88	56:44[e]
				93	0:100[e,f]
2	p-MeC_6H_4	86	88:12	82	56:44[e]
				77	0:100[e,f]
3	$PhCH_2$	80	90:10	73	59:41
4	p-$NO_2C_6H_4$	80	85:15	71	67:33
5	p-ClC_6H_4	88	88:12	85	60:40
6	Hexyl	78	89:11	84	52:48
7	Cyclohexyl	84	89:11	80	55:45
8	t-Butyl	54	90:10	56	52:48
9	i-Butyl	80	90:10	82	55:45

[a] 3eq.CB/3% $ClRh(PPh_3)_3$/THF, r.t., 24 h.; [b] 3eq.BH_3/THF, r.t., 24 h.; [c] isolated yield; [d] determined by 300 MHz ^1H-NMR, all new compounds have satisfactory analytic results; [e] ref.11; [f] 9-BBN was used.

From Table 1, it could be found that the yield of catalysed hydroboration was same as conventional hydroboration[11], but the regioselectivity of two types of reaction was very different. The regiochemistry of conventional hydroboration of allyl derivatives is strongly influenced by the allylic substituted group. For example, about 20% boron atom attached the secondary position for an ethoxy substituent and 40% for a chlorine substituent when BH_3 was used[1]. More boron atom attached the primary position if dialkylboranes were used, and similar selectivity was showed when CB was used as reagent[1]. In the case of SO_2 group there was almost no regioselectivity (Table 1)[11]. The ratio of (**2**) and (**3**) for conventional hydroboration was between 1.1 and 1.99 to 1, for catalysed hydroboration it was between 6 and 9 to 1. On the other hand when 9-BBN was used as reagent the reaction provided (**3**) as sole product (entry 1,2)[11]. These results showed that SO_2 group might play a role as directing group through complexing with rhodium. Thus all substrates gave almost same results in spite of different electronic or steric effects of the R group. Evans[5] and Burgess[12] showed that the regioselectivities were different if "aged" or "fresh" catalyst was used. In our case, the life of the catalyst had only a small influence on the results[13]. Lastly the solvent had some effect on the regioselectivity. If the reaction was run in THF, CH_2Cl_2 or benzene the regioselectivity was decreased sequentially.

In conclusion, hydroboration of allyl sulfones can be catalysed by Wilkinson's catalyst effectively to furnish secondary hydroxy compounds with good regioselectivity. It is the first time that metal catalysed hydroboration of terminal alkenes gives rise to Markownikoff products. Because of the usefulness of sulfone compounds[14], this reaction would be applied in organic synthesis. Now the research for metal catalysed hydroboration of other heteroatom substituted allyl derivatives is in progress.

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References:

1. Pelter,A.; Smith,K.; Brown,H.C. Borane Reagents, Academic Press:

London, 1988.

2. Mannig,D.; Noth,H. Angew.Chem., Int.Ed.Engl. **1985**,24,878.
3. Burgess,K.; Ohlmeyer,M.J. Chem.Rev. **1991**,91,1179.
4. Evans,D.A.; Fu,G.C.; Hoveyda,A.H. J.Am.Chem.Soc. **1992**,114,6671.
5. Evans,D.A.; Fu,G.C.; Anderson,B.A. J.Am.Chem.Soc. **1992**,114,6679.
6. a)Evans,D.A.; Fu,G.C.; Hoveyda,A.H. J.Am.Chem.Soc. **1988**,110,6917.
   b)Sato,M.; Miyaura,N.; Suzuki,A. Tetrahedron Lett. **1990**,31,231.
   c)Brown,J.M.; Lloyd-Jones,G. Tetrahedron: Asymmetry **1990**,1,869.
   d)Burgess,K.; Cassidy,J.; Ohlmeyer,M.J. J.Org.Chem. **1991**,56,1020.
   e)Burgess,K.; Donk,W.A.van der; Ohlmeyer,M.J. Tetrahedron: Asymmetry **1991**,2,613.
7. Hayashi,T.; Matsumoto,Y.; Ito,Y. J.Am.Chem.Soc. **1989**,111,3426.
8. a)Zhang,J.; Lou,B.; Guo,G.; Dai,L. J.Org.Chem. **1991**,56,1670.
   b)Zhang,J.; Lou,B.; Guo,G.; Dai,L. Acta Chim.Sin. **1992**,50,913.
9. Westcott,S.A.; Blom,H.P.; Marder,T.B.; Baker,R.T. J.Am.Chem.Soc. **1992**,114,8863.
10. a)Crandall,J.K.; Pradat,C. J.Org.Chem. **1985**,50,1327.
    b)Issari,B.; Stirling,C.J.M. J.Chem.Soc., Perkin Trans.II **1984**, 1043.
11. Moreau,R.; Adam,Y.; Loiseau,P. C.R.Acad.Sc.Paris, Serie C **1978**, 39.
12. Burgess,K.; Donk,W.A.van der; Westcott,S.A.; Marder,T.B.; Baker,R.T.; Calabress,J.C. J.Am.Chem.Soc. **1992**,114,9350.
13. The catalyst newly purchased from Aldrich or with long shelf life gave almost the same results.
14. Simpkins,N.S. Sulphones in Organic Synthsis, Pergamon: Oxford, 1993.

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