

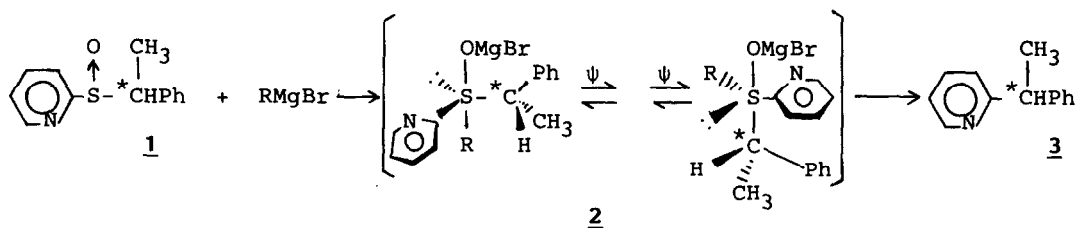
LIGAND COUPLING THROUGH σ -SULFURANE --- COMPLETE RETENTION OF
GEOMETRIC CONFIGURATION OF ALLYLIC AND VINYLIC GROUPS IN THE REACTIONS
OF ALLYLIC AND VINYLIC SULFOXIDES WITH GRIGNARD REAGENTS

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Abstract: The reaction of p-benzenesulfonylphenyl crotyl sulfoxide with Grignard reagents is considered to proceed via formation of an incipient σ -sulfurane to afford the coupling product, p-benzenesulfonyl-crotylbenzene, in which the geometric configuration of crotyl group was completely preserved. No rearrangement was observed in the coupling reaction of p-benzenesulfonylphenyl α -methylallyl sulfoxide. Such a complete retention of geometric configuration was also found in the reactions of 2-pyridyl and p-benzenesulfonylphenyl styryl sulfoxides with Grignard reagents.

Earlier, we have shown that the reaction of optically active 1-phenylethyl 2-pyridyl sulfoxide(**1**) with either phenyl or methyl Grignard reagent afforded the corresponding optically active coupling product, i.e., 2-(1-phenylethyl)-pyridine(**3**), in which the configuration of 1-phenylethyl group was completely retained.¹⁾ We then postulated that the reaction proceeds via formation of a sulfurane intermediate(**2**), formed upon the nucleophilic attack of the Grignard reagent and subsequent coupling of 2-pyridyl group and 1-phenylethyl group after pseudorotation as shown below.²⁾



This stereochemical experiment clearly revealed that the ligand coupling within the incipient σ -sulfurane is a concerted process.

Meanwhile, we have found that phenyl group bearing an electron-withdrawing group, such as p-benzenesulfonylphenyl group, similarly to 2-pyridyl group, can also couple readily with either benzylic or allylic group in the reaction of benzylic³⁾ or allylic sulfoxides with Grignard reagents. However, the vinylic group was found to couple with p-benzenesulfonylphenyl group or 2-pyridyl group

less readily than benzylic group. The order of coupling reactivity was observed to be benzylic group \gg allylic group $>$ vinylic group (Entry 4,5,8 and 10), as can be seen in Table 1.

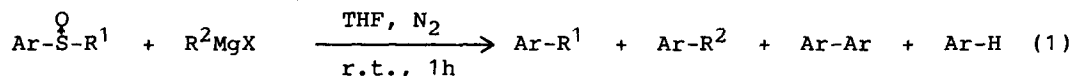


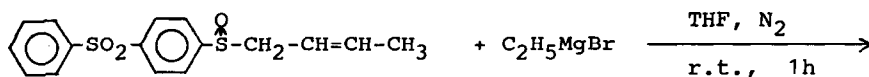
Table 1. The products in the reaction(1) of a few aryl allylic and vinylic sulfoxides with various Grignard reagents

Entry	Ar	R ¹	R ²	Products yield/% a)			
				Ar-R ¹	Ar-R ²	Ar-Ar	Ar-H
1	p-Bsp	CH ₂ =CHCH ₂	C ₂ H ₅	53.0	-	-	-
2	"	CH ₂ =C(CH ₃)CH ₂	C ₂ H ₅	63.7	-	-	-
3	"	PhCH=CH	Ph	15.3	-	-	35.4
4	"	C ₂ H ₅	CH ₂ =CHCH ₂	-	45.1	-	-
5	"	C ₂ H ₅	PhCH=CH	-	-	-	21.5
6	"	C ₂ H ₅	CH ₃ CH=CH	-	-	-	42.7
7	"	PhCH ₂	CH ₂ =CHCH ₂	51.3	-	-	-
8	"	CH ₂ =CHCH ₂	PhCH ₂	-	73.1	-	-
9	"	PhCH ₂	PhCH=CH	42.2	-	-	-
10	"	PhCH=CH	PhCH ₂	-	50.0	-	-
11	"	PhCH ₂	CH ₃ CH=CH	53.1	-	-	-
12	2-Py	PhCH=CH	C ₂ H ₅	41.0	-	-	-
13	"	C ₂ H ₅	PhCH=CH	-	-	5.1	-
14	"	C ₂ H ₅	CH ₃ CH=CH	-	-	6.2	-
15	"	PhCH=CH	PhCH ₂	-	44.0	-	-
16	"	PhCH ₂	PhCH=CH	42.0	-	-	-
17	"	PhCH ₂	CH ₃ CH=CH	43.3	-	-	-

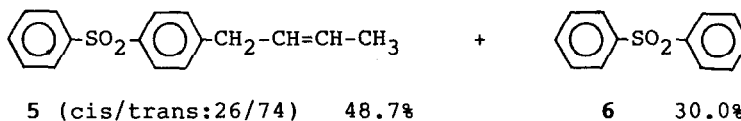
Bsp: benzenesulfonylphenyl ; Py: pyridyl ; a) Isolated yield ;
b) Reaction Time : 2h ; c) 5h

Especially interesting would be the stereochemical observation on the reactions of both p-benzenesulfonylphenyl crotyl sulfoxide and p-benzenesulfonylphenyl or 2-pyridyl styryl sulfoxide with Grignard reagents, since one can readily observe the change of geometrical configuration of crotyl or styryl group, if any dissociation or sigmatropic rearrangement would occur during the reaction. Meanwhile, if the coupling of crotyl or styryl group with p-benzenesulfonylphenyl and 2-pyridyl groups proceeds concertedly within the sulfurane formed by the attack of a Grignard reagent on the sulfoxide, we would observe that the geometric configuration of the allylic or vinylic group in the resulted coupling product is completely retained throughout the reaction.

Thus, we have first carried out the following reaction with ethylmagnesium bromide of p-benzenesulfonylphenyl crotyl sulfoxide(4), in which the cis-trans ratio of crotyl group is 26 : 74.



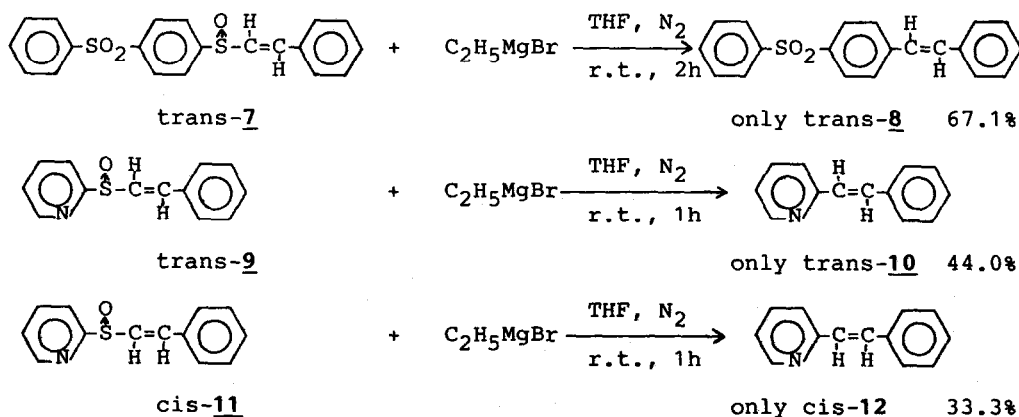
4 (cis/trans:26/74)



This reaction afforded two products, p-benzenesulfonyl-crotylbenzene(5) and diphenylsulfone(6). Obviously the former 5 is resulted by ligand coupling and the latter 6 is formed by ligand exchange reaction respectively. However, the major product was ligand coupling product 5, which was found to have retained exactly in the same cis/trans geometrically isomeric ratio of crotyl group, namely 26 : 74, as determined by ^1H NMR spectra, i.e., $\delta=1.37$ (d, $J=7\text{Hz}$, 0.78H, cis- CH_3): 1.66 [d, $J=5\text{Hz}$, 2.22H, trans- CH_3) and 1.39 (d, $J=7\text{Hz}$, 0.77H, cis- CH_3): 1.64 [d, $J=5\text{Hz}$, 2.23H, trans- CH_3) of crotyl groups of both the starting sulfoxide and the resulted coupling product⁴).

Here again, the ratio of cis-trans of crotyl group remained throughout the coupling reaction.

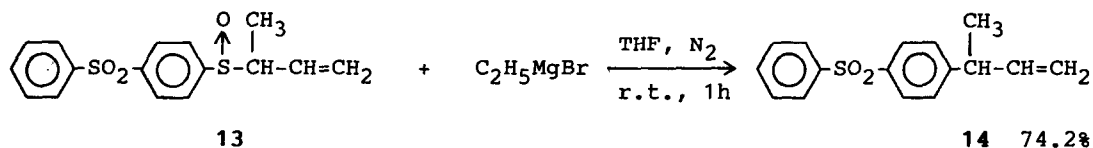
Next, the reactions of p-benzenesulfonylphenyl and 2-pyridyl styryl sulfoxides with ethylmagnesium bromide were carried out as shown below.



The reaction of trans-p-benzenesulfonylphenyl styryl sulfoxide(7) afforded only trans-p-benzenesulfonyl-stylbene(8) in a good yield.⁵) Further, the coupling reactions of trans- and cis-2-pyridyl styryl sulfoxide(9 and 11)⁶) with the Grignard reagent gave also the corresponding coupling product, trans-2-styrylpyridine(10) and cis-2-styrylpyridine(12)⁷), respectively. In order to confirm the geometric configuration of coupling product, 8 and 10 were subjected to X-ray crystallographic analysis, which indeed have been confirmed to be of pure trans form.⁸) Thus, the geometrical configuration of the double bond in the sulfoxide did not change in the ligand coupling reaction.

A similar reaction was carried out with p-benzenesulfonylphenyl α -methylallyl sulfoxide(13) with ethylmagnesium bromide, since any dissociation or isomerization would cause some isomerization of α -methylallyl group bearing the

ligand coupling. The ligand coupling between the aryl group and α -methylallyl group proceeded smoothly as shown below.



The coupling product was p-benzenesulfonyl- α -methylallylbenzene (**14**) alone and no rearranged crotyl derivative was observed in the product.

These observations suggest clearly again that the ligand coupling within the σ -sulfurane is a concerted process.

References

- 1) S.Oae, T. Kawai, and N. Furukawa, *Tetrahedron Lett.*, **25**, 69 (1984); S. Oae, T. Kawai, N. Furukawa, and F. Iwasaki, *J.Chem.Soc. Perkin Trans.II*, **1987**, 405.
- 2) S. Oae, *Croat. Chem. Acta*, **59**, 129 (1986); S. Oae, *Phosphorus and Sulfur*, **27**, 13 (1986).
- 3) T. Kawai, Y. Kotera, N. Furukawa, S. Oae, M. Ishida, T. Takeda, and S. Wakabayashi, *Phosphorus and Sulfur*, **34**, 139 (1987).
- 4) **4**: Mp 95.0-96.0°C; $^1\text{H NMR}$ (CDCl_3) δ =1.37 (d, J =7Hz, 0.78H, cis- CH_3), 1.66 (d, J =5Hz, 2.22H, trans- CH_3), 3.38-3.91 (m, 2H), 5.31-5.59 (m, 2H), 7.11-8.21 (m, 9H). **5**: Mp 69.0-70.0°C; $^1\text{H NMR}$ (CDCl_3) δ =1.39 (d, J =7Hz, 0.77H, cis- CH_3), 1.64 (d, J =5Hz, 2.23H, trans- CH_3), 3.09-3.70 (m, 2H), 4.70-6.15 (m, 2H), 7.06-8.35 (m, 9H).
- 5) **7**: Mp 141.3-143.0°C; $^1\text{H NMR}$ (CDCl_3) δ =6.80 (d, J =16Hz, 1H, trans = CH), 7.10-8.35 (m, 15H). **8**: Mp 188.9-190.0°C; $^1\text{H NMR}$ (CDCl_3) δ =7.00 (d, J =17Hz, 1H, trans = CH), 7.10-7.75 (m, 11H), 7.75-8.10 (m, 4H).
- 6) **9**: Mp 74.2-74.9°C; $^1\text{H NMR}$ (CDCl_3) δ =6.98 (d, J =16Hz, 1H, trans = CH), 7.16-8.48 (m, 9H), 8.48-8.75 (m, 1H). **11**: Mp 63.7-64.1°C; $^1\text{H NMR}$ (CDCl_3) δ =6.37 (d, J =10Hz, 1H, cis = CH), 6.88-8.43 (m, 9H), 8.43-8.83 (m, 1H).
- 7) **10**: Mp 89.5-90.0°C; **12**: pale yellow oil. Isomeric purity of each coupling product was confirmed by comparison of X-ray diffraction patterns and retention time in gas chromatography.
- 8) The X-ray crystallographic analysis was carried out by the courtesy of Dr. T. Numata of Takeda Pharm. Chem. Ind. and Professor T. Shibahara of Okayama University of Science.

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