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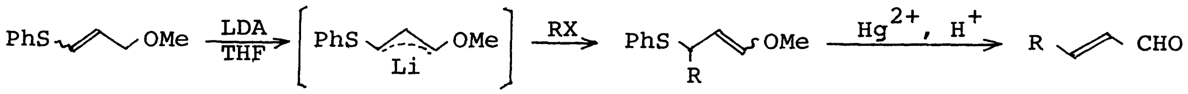
1-ARYLSULFINYL-1-ALKEN-1-YLLITHIUM

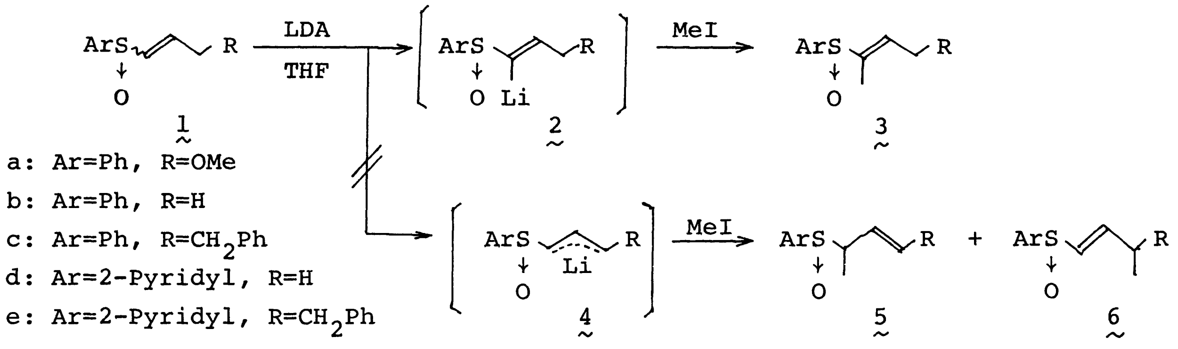
Hisashi OKAMURA, Yoshiyuki MITSUHIRA, Morikazu MIURA, and Hisashi TAKEI
Department of Life Chemistry, Tokyo Institute of Technology,
Nagatsutacho, Midori-ku, Yokohama 227

The generation of the title compound(**2**) by the treatment of alkenyl aryl sulfoxide(**1**) with lithium diisopropylamide (LDA), and the reactions of **2** with methyl iodide, carbonyl compounds, and oxiranes were described.

Recently, it was found in our laboratory that 3-methoxy-1-(phenylthio)propene could be alkylated exclusively at the α-position of the sulfur atom <u>via</u> the allylic lithium derivative and the alkylated products afforded α,β-unsaturated aldehydes in good yields by hydrolysis in the presence of mercuric chloride.$^{1)}$

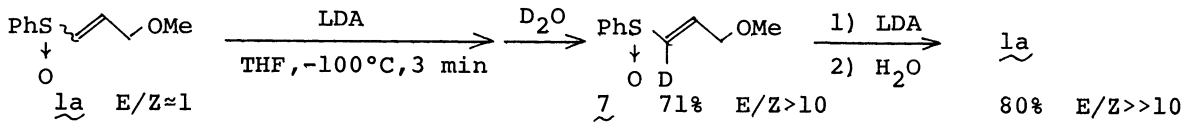


We now examined the alkylation of a similar compound(**1a**)$^{2)}$ having a phenylsulfinyl group as an anion stabilizing group. Contrary to the above lithiation of the sulfide,$^{1,3)}$ it was found that a 1-propene-1-yllithium derivative(**2a**) was formed by the treatment of **1a** with LDA, and the subsequent treatment with methyl iodide gave 4-methoxy-2-phenylsulfinyl-2-butene(**3a**) in 73% yield. In this experiment, both sulfoxides **5a** and **6a** could not be detected.



a: Ar=Ph, R=OMe
b: Ar=Ph, R=H
c: Ar=Ph, R=CH_2Ph
d: Ar=2-Pyridyl, R=H
e: Ar=2-Pyridyl, R=CH_2Ph

In order to prove the formation of the 1-propen-1-yllithium derivative(**2a**) as an intermediate of this reaction, the following experiments were carried out. First, the anion generated from **1a** was quenched with D_2O. The product was found to be an α-deuterated sulfoxide(**7**) and none of the product deuterated at the allylic position was detected. The resulted **7** was then treated with LDA and the reaction was quenched with H_2O. The product, **1a**, did not have any deuterium at the α-position. On the basis of these results, it can be concluded that **2a** is the real intermediate.



Similarly, sulfoxides(**1b**–**e**)4) could be converted into 1-alken-1-yllithium derivatives(**2b**–**e**) and the resulted **2** reacted with methyl iodide to afford 2-alken-2-yl sulfoxides(**3b**–**e**).5) These results are summarized in Table 1. When 2-pyridyl sulfoxides were used (runs 12, 13, and 14), the methylated products were obtained in excellent yields. In these cases, the lithium derivatives may exist as 5-membered chelates(**8**) similar to the case of allyl pyridyl sulfide.6)

Table 1. Lithiation and methylation of alkenyl sulfoxides(**1**)

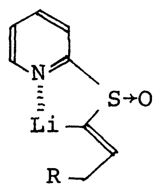
Run	**1**	Ar	R	E/Z a)	Lithiation conditions Temp.(°C)	Time(min)	**3**	E/Z a)	Yields b) (%)
1	**1a**	Ph	OMe	1	-100	≈10 sec	**3a**	c)	63
2	**1a**	Ph	OMe	1	-100	2	**3a**	4	72
3	**1a**	Ph	OMe	1	-100	5	**3a**	≫10	73
4	**1a**	Ph	OMe	1	-78	≈10 sec	**3a**	≫10	70
5	**1a**	Ph	OMe	1	-78	2	**3a**	≫10	53
6	**1a**	Ph	OMe	1	-78	15	**3a**	≫10	53
7	**1b**	Ph	H	1	-100	5	**3b**	4	84
8	**1b**	Ph	H	1	-100	10	**3b**	≫10	80
9	**1b**	Ph	H	1	-100	90	**3b**	≫10	51
10	**1c**	Ph	CH_2Ph	1	-100	10	**3c**	>10	89
11	**1c**	Ph	CH_2Ph	0	-100	10	**3c**	>10	79
12	**1d**	2-Pyridyl	H	1.5	-78	2	**3d**	≫10	93
13	**1d**	2-Pyridyl	H	1.5	-100	5	**3d**	≫10	96
14	**1e**	2-Pyridyl	CH_2Ph	2	-100	5	**3e**	≫10	99

a) The ratio was determined by nmr.7) b) Yields of isolated products.

c) The ratio was not determined.

The following experiment provides a typical procedure for the generation of the lithium derivatives of alkenyl sulfoxides and the subsequent methylation reaction: A THF (3 ml) solution of **1a** (1 mmol) was added to a THF (3 ml) solution of LDA (1.2 mmol) prepared from diisopropylamine and butyllithium under an argon atmosphere at -100°C. After stirring for 5 min at -100°C followed by the addition of excess methyl iodide and further stirring for 30 min at the same temperature, the reaction mixture was quenched with an aqueous ammonium chloride solution. Usual work-up and the purification using silica gel tlc afforded **3a** in 73% yield.

Stereochemistry of the reaction is particularly noteworthy. Comparing of the ratio of (E)- and (Z)-isomers of the starting materials with that of the products, it is clear that cis-trans isomerization took place easily at the state of the anions even at -100°C. The preferential formation of the (E)-isomer may be due to the steric repulsion between the arylsulfinyl group and the substituent attached to the β-carbon, though the chelate effect represented as **9** may play an important role in the case of **1a**.8) On the other hand, it is well known that simple alkenyl anions generally exhibit very high degree of retention of configurations.9) Easy cis-trans isomerization observed in this study can be explained by the effect of the arylsulfinyl group which may lower the energy barrier for the isomerization.8)



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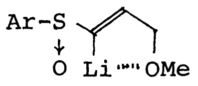

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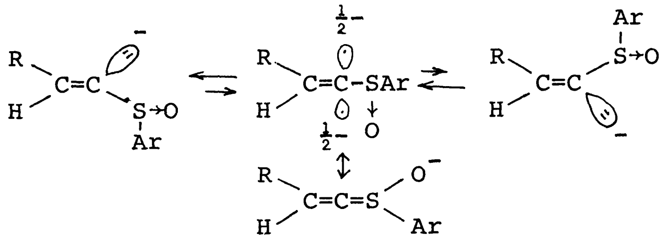


Next, we examined the alkylation of the anions using butyl iodide or benzyl bromide, but the yield was low (11% or 24%, respectively). The reaction of the anions with carbonyl compounds gave the adducts(**10**) in good yields. Similarly **2** afforded the adducts(**11** or **12**) with oxiranes. Some of these results are listed in Table 2.

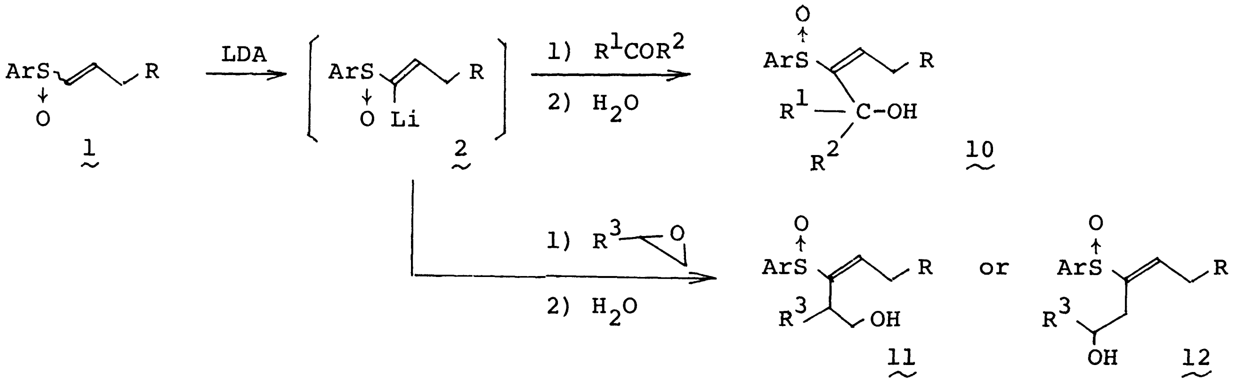
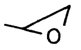
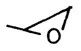


Table 2. Reactions of alkenyl sulfoxides(**1**) with carbonyl compounds and oxiranes

1		Electrophile	Lithiation reaction		Addition reaction		Adduct		
	E/Za)		Temp.(°C)	Time(min)	Temp.(°C)	Time(min)		Yield(%)	E/Za)
1a	1	PhCHO	-100	3	-78	75	**10**	80	>10
1a	1	PhCOMe	-100	5	-78	40	**10**	74	5
1b	1	PhCHO	-100	10	-100	30	**10**	93	≈10
1d	2	PhCHO	-100	5	-100	30	**10**	91	≫10
1b	1	Ph	-100	12	-78	60	**11**	23	≫10
1b	1	Me	-78	2	-40	40	**12**	45	≫10

a) The ratio was determined by nmr.

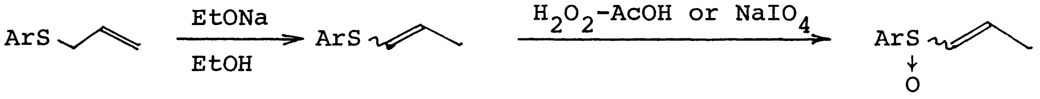
References and Notes

1) M. Wada, H. Nakamura, T. Taguchi, and H. Takei, Chem. Lett., 1977, 345.

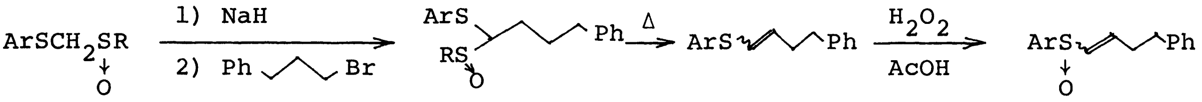
2) The sulfoxide(1a) was synthesized in 88% yield by oxidation of the corresponding sulfide.

3) 3-Allyloxy-1-phenylthiopropene also forms an allylic lithium derivative; M. Wada, A. Fukui, H. Nakamura, and H. Takei, Chem. Lett., 1977, 557.

4) These sulfoxides[5)] were synthesized according to the following scheme;



1b:	Ar=Ph	89%	96%
1d:	Ar=2-Pyridyl	88%	78%



1c:	Ar=Ph, R=Ph	81%	88%	93%
1e:	Ar=2-Pyridyl, R=Me	85%	96%	89%

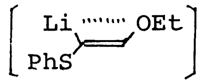
5) All new compounds gave satisfactory elemental analysis, and nmr and ir spectra of them well agreed with the assigned structures.

6) T. Mukaiyama, K. Narasaka, K. Maekawa, and M. Furusato, Bull. Chem. Soc. Jpn., 44, 2285 (1971); K. Narasaka, M. Hayashi, and T. Mukaiyama, Chem. Lett., 1972, 259.

7) The ratio of E/Z was determined by nmr mainly based on the β-proton listed in the following Table.

Chemical shift of β-proton of 1 and 3

Compound	δ (CCl_4)		Compound	δ (CCl_4)	
	E	Z		E	Z
1a	6.45	6.17	3a	6.43	5.98
1b	6.48	≈6.1	3b	6.40	5.90
1c	6.65	6.10	3c	6.35	≈6.0
1d	6.40	≈6.2	3d	6.42	
1e	6.43	≈6.1	3e	6.53	

8) Similar chelation and isomerization of the lithio derivative of ethoxyvinyl phenyl sulfide  have been reported; I. Vlattas, L. D. Vecchia, and A. O. Lee, J. Am. Chem. Soc., 98, 2008 (1976).

9) D. Y. Curtin and J. W. Crump, J. Am. Chem. Soc., 80, 1922 (1958); H. M. Walborsky and L. M. Turner, ibid., 94, 2273 (1972), and references cited therein.

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