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The Michael Type Alkylation of α,β-Unsaturated Sulfoxide and Reaction of the Resulting α-Sulfinyl Carbanion

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Synopsis. Aryl vinyl sulfoxide was alkylated *via* the Michael-type addition with lithium dialkylcuprates, and the resulting α-sulfinyl carbanions were reacted with various electrophiles (*i.e.* aldehydes, ketones, and alkyl halides) to afford α-substituted alkyl sulfoxides.

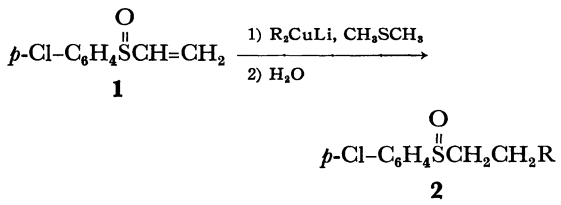
α,β-Unsaturated sulfoxides undergo Michael-type addition in the presence of a base.[1] However, no Michael-type alkylation to α,β-unsaturated sulfoxides has been investigated,[2] only a few reactions of secondary α-sulfinyl carbanions being reported.[3]

This paper describes the Michael-type alkylation to aryl vinyl sulfoxides, and the reaction of the initially formed α-sulfinyl carbanions with various electrophiles in one pot.

Results and Discussion

p-Chlorophenyl vinyl sulfoxide (**1**) was polymerised by alkyllithium, and was inert with the Grignard reagents.

On the other hand, vinyl sulfoxide **1** was alkylated by lithium dimethylcuprate, lithium dibutylcuprate and lithium di-*t*-butylcuprate to give *p*-chlorophenyl propyl sulfoxide (**2a**), *p*-chlorophenyl hexyl sulfoxide (**2b**), and *p*-chlorophenyl 3,3-dimethylbutyl sulfoxide (**2c**), respectively.



In the above Michael-type reaction, α-sulfinyl carbanion (**3**) was trapped by various electrophiles. β-Hydroxy sulfoxides (**4a**, **b**, **c**) were obtained when benzophenone was added to a solution of **3**. No 1,2-adduct of benzophenone was obtained even when benzophenone and **1** were added to lithium dialkylcuprate at the same time.[4]

Enolizable ketones and aldehydes such as cyclohexanone and propionaldehyde were treated in the same way to give the corresponding condensation products (**4e**, **f**) and **2b**.

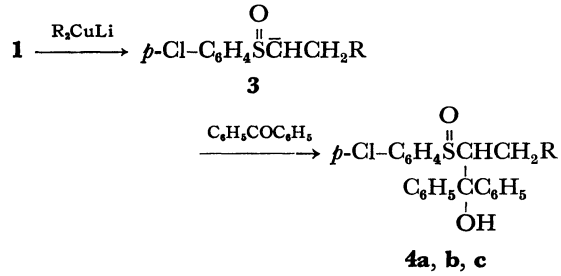
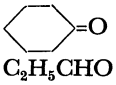
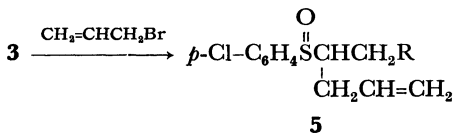


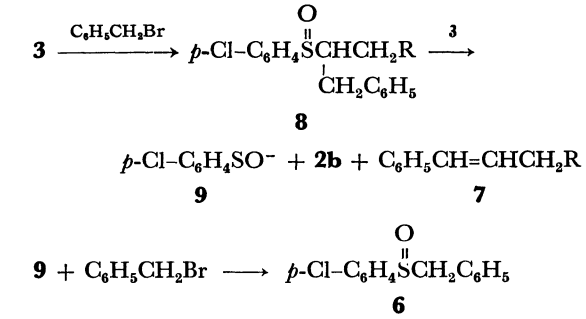
Table 1. Reaction of α-sulfinyl carbanion with electrophiles (yield of **2**, **4**, **5**)

Electrophile	R_2CuLi R= CH_3	n-C_4H_9	t-C_4H_9
H^+	30	75	34
$(C_6H_5)_2CO$	80	73	45
C_6H_5CHO	—	67	—
	—	26	—
C_2H_5CHO	—	13	—
CH_2=$CHCH_2Br$	—	73	—

Allyl bromide underwent substitution reaction with **3** to afford *p*-chlorophenyl 1-allylhexyl sulfoxide (**5**). The results are given in Table 1.



Benzyl *p*-chlorophenyl sulfoxide (**6**), **2b** and 1-phenyl-1-heptene (**7**) were obtained when benzyl bromide was treated in the same way. It is assumed that **3** reacts with benzyl bromide to give alkylated sulfoxide (**8**), and the first formed **8** easily eliminates sulfenate (**9**) under basic conditions to give **7**,[5] the residual benzyl bromide combining with liberated **9** to produce **6**.



Experimental

Alkylation of p-*Chlorophenyl Vinyl Sulfoxide* ***1.***

p-*Chlorophenyl Propyl Sulfoxide* ***2a***: To an ether–dimethyl sulfide (1: 1, v/v) solution (30 ml) of copper(I) bromide–dimethyl sulfide complex[6] (1.03 g, 5 mmol) was added an ethereal solution of methyllithium (9 mmol) at 0 °C under nitrogen. The solutions was cooled to −60 °C, and **1** (1.31 g, 7 mmol) in ether (10 ml) was added. The temperature of the

mixture was allowed to rise to room temperature. The mixture was then extracted with ether, and dried over magnesium sulfate dehydrate. After removal of the solvent, **2a** was isolated (0.43 g, 30%) by chromatography on silica gel; oil: IR (film) 1030 (S=O) cm^{-1}; NMR (CCl_4) δ=1.02 (3H, t, J=7 Hz), 1.60 (2H, m), 2.64 (2H, t, J=7 Hz), 7.45 (4H, m).

p-*Chlorophenyl Hexyl Sulfoxide* ***2b***: To a solution of the copper(I) bromide complex (5 mmol) was added a hexane solution of butyllithium (9 mmol) at −60 °C under nitrogen. After being left to stand for 30 min, **1** (7 mmol) in ether was added to the mixture. The temperature of the mixture was allowed to rise to room temperature. After the usual work-up **2b** was isolated (1.28 g, 75%) by chromatography on silica gel: oil; IR (film) 1030 (S=O) cm^{-1}; NMR (CCl_4) δ=0.87 (3H, m), 1.30 (8H, m), 2.72 (2H, t, J=7 Hz), 7.48 (4H, m).

p-*Chlorophenyl 3,3-Dimethylbutyl Sulfoxide* ***2c***: To a solution of the copper(I) bromide complex (5 mmol) was added a pentane solution of *t*-butyllithium (9 mmol) at −78 °C under nitrogen. After being left to stand for 30 min, **1** (7 mmol) was added to the mixture. After the usual work-up **2c** (0.57 g, 34%) and *p*-chlorophenyl 1,1-dimethylethyl sulfoxide (0.17 g, 11%) were isolated by chromatography on silica gel. **2c**: mp 65—68 °C; IR (KBr) 1030 (S=O) cm^{-1}; NMR (CCl_4) δ=0.90 (9H, s), 1.50 (2H, m), 2.68 (2H, m), 7.50 (4H, m). *p*-Chlorophenyl 1,1-dimethylethyl sulfoxide: oil; IR (film) 1030 (S=O) cm^{-1}; NMR (CCl_4) δ=1.08 (9H, s), 7.45 (4H, m).

Reaction of α-Sulfinyl Carbanion ***3*** *with Electrophiles.*

p-*Chlorophenyl 1-(Diphenylhydroxymethyl)propyl Sulfoxide* ***4a***: To a solution of lithium dimethylcuprate was added an ethereal solution of **1** (7 mmol) and benzophenone (7 mmol) at −60 °C under nitrogen. The temperature of the mixture was allowed to rise to room temperature. After the usual work-up **4a** (2.16 g, 80%) was obtained: mp 129—131 °C; IR(KBr) 3420 (OH), 1005 (S=O) cm^{-1}; NMR ($CDCl_3$) δ= 0.20 (3H, t, J=7 Hz), 1.80 (2H, m), 3.42 (1H, m), 4.65 (1H, m), 7.42 (14H, m).

p-*Chlorophenyl 1-(Diphenylhydroxymethyl)hexyl Sulfoxide* ***4b***: To a solution of lithium dibutylcuprate was added an ethereal solution of **1** (7 mmol) and benzophenone (7 mmol) at −60 °C. The temperature of the mixture was allowed to rise to room temperature. After the usual work-up **4b** (2.18 g, 73%) was obtained: mp 120—121 °C; IR (KBr) 3420 (OH), 1000 (S=O) cm^{-1}; NMR ($CDCl_3$) δ=0.70 (9H, m), 1.76 (2H, m), 3.43 (1H, m), 7.40 (15H, m).

p-*Chlorophenyl 3,3-Dimethyl-1-(diphenylhydroxymethyl)butyl Sulfoxide* ***4c***: To a solution of lithium di-*t*-butylcuprate was added an ethereal solution of **1** (7 mmol) and benzophenone (7 mmol) at −78 °C. The mixture was treated in a similar way as described in the previous section, and **4c** (1.35 g, 45%) was obtained: mp 119—120 °C; IR (KBr) 3420 (OH), 1005 (S=O) cm^{-1}; NMR ($CDCl_3$) δ=0.12 (7.7 Hz, s), 0.90 (1.3H, s), 1.80 (2H, m), 3.35 (1H, t, J=4 Hz), 4.95 (1H, m), 7.34 (14H, m).

p-*Chlorophenyl 1-(α-Hydroxybenzyl)hexyl Sulfoxide* ***4d***: To a solution of lithium dibutylcuprate was added an ethereal solution of **1** (7 mmol) at −60 °C under nitrogen, an ethereal solution of benzaldehyde (7 mmol) being added after having been left to stand for 30 min. The mixture was then treated in a similar way as described in the section for **4c**, and **4d** (diastereomers) (1.57 g, 67%) were isolated by chromatography on silica gel: mp 80—82 °C; IR (KBr) 3420 (OH), 1000 (S=O) cm^{-1}; NMR ($CDCl_3$) δ=0.80 (11H, m), 1.62 (1H, m), 2.70 (1H, m), 4.80 (1H, d, J=8 Hz), 7.22 (9H, m): mp 103—105 °C; IR (KBr) 3420 (OH), 1000 (S=O) cm^{-1}; NMR ($CDCl_3$) δ=0.80 (11H, m), 1.62 (1H, m), 2.70 (1H, m), 5.22 (1H, d, J=4 Hz), 7.22 (9H, m).

p-*Chlorophenyl 1-(1-Hydroxycyclohexyl)hexyl Sulfoxide* ***4e***: Cyclohexanone (7 mmol) was treated in a similar way as described in the preceding sections **4e** (0.62 g, 26%) and **2b** (0.64 g, 37%) were isolated by chromatography on silica gel. **4e**: mp 130—132 °C; IR (KBr) 3420 (OH), 1005 (S=O) cm^{-1}; NMR ($CDCl_3$) δ=1.20 (21H, m) 2.62 (1H, t, J=4 Hz), 4.23 (1H, s), 7.50 (4H, m).

p-*Chlorophenyl 1-(1-Hydroxypropyl)hexyl Sulfoxide* ***4f***: Propionaldehyde (7 mmol) was treated in a similar way as described in the preceding sections, **4f** (0.26 g, 13%) and **2b** (0.63 g, 37%) were isolated. **4f**: oil; IR (film) 3420 (OH), 1005 (S=O) cm^{-1}; NMR (CCl_4) δ=1.20 (17H, m), 2.42 (1H, m), 3.78 (1H, m), 7.48 (4H, m).

p-*Chlorophenyl 1-Allylhexyl Sulfoxide* ***5***: Allyl bromide (7 mmol) was treated in a similar way as described in the preceding sections, **5** (1.45 g, 73%) was obtained: oil; IR (film) 1030 (S=O) cm^{-1}; NMR (CCl_4) δ=1.40 (14H, m), 5.00 (2H, m), 5.52 (1H, m), 6.45 (4H, m).

Reaction of ***3*** *with Benzyl Bromide*: Benzyl bromide (7 mmol) was treated in a similar way as described in the preceding sections. After the work-up, **2b** (0.40 g, 47%), benzyl *p*-chlorophenyl sulfoxide **6** (0.40 g, 46%) and 1-phenyl-1-hexene **7** (0.25 g, 41%) were isolated by chromatography on silica gel. **6**: mp 133—134 °C; IR (KBr) 1030 (S=O) cm^{-1}; NMR ($CDCl_3$) δ=4.03 (2H, d, J=4 Hz), 7.24 (5H, m). **7**: oil; NMR (CCl_4) δ=0.92 (3H, m), 1.38 (6H, m), 2.20 (2H, m), 6.20 (2H, m), 7.17 (5H, m).

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