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PREPARATION AND REARRANGEMENT OF 2-ALLYLOXYETHYL ARYL SULFOXIDES; A MERCURY-FREE CLAISEN SEQUENCE

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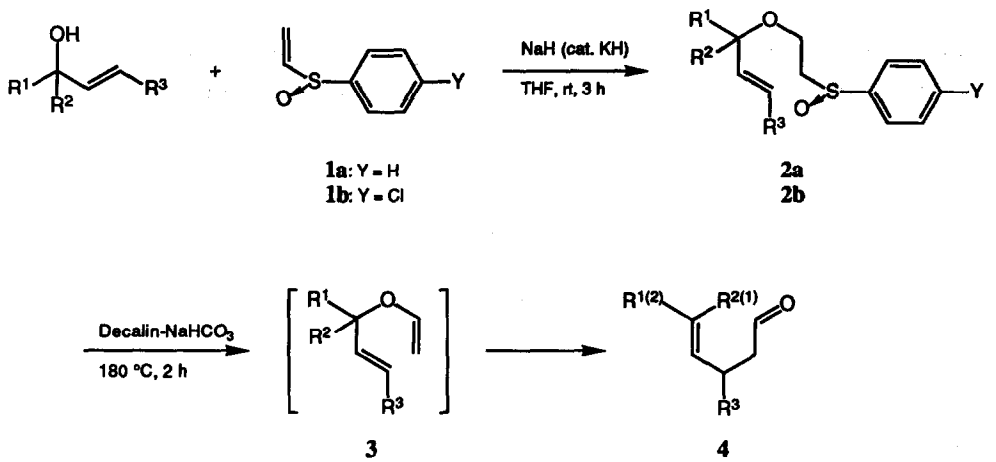
Summary: Alkali metal hydride promoted addition of allylic alcohols to aryl vinyl sulfoxides at room temperature gives 2-allyloxyethyl aryl sulfoxides, which, on heating, are converted into γ,δ-unsaturated aldehydes via allylic vinyl ethers.

Claisen rearrangement of allylic vinyl ethers is a very important synthetic transformation and has widely been used in organic synthesis.[1] Allylic vinyl ethers are prepared in general from allylic alcohols by the vinyl ether exchange reaction with alkyl vinyl ethers. Mercuric salts are regarded as one of the most effective promoters for this purpose. However, the use of toxic mercuric salts in a large amount is not tolerable in these days. In addition, a large excess of ethyl vinyl ethers is required and results are not always reliable, particularly with regard to sterically congested allylic alcohols. Thus, an efficient mercury-free preparative method is highly desirable.

Buchi and Vogel developed a new Claisen sequence, as a mercury-free process, via trans-3-alkoxyacrylic acids synthesized by the reaction of allylic alcohols with the betaine derived from ethyl propiolate and trimethylamine.[2] Although their method is promising for primary and secondary allylic alcohols, it can not be applied to tertiary allylic alcohols.[2]

In our rigorous efforts to develop a new mercury-free method which is applicable to tertiary allylic alcohols, we noticed a hidden potential of 2-allyloxyethyl phenyl sulfoxide **2a** as a new precursor of allyl vinyl ethers **3**.[3] We expected that Michael-type addition of allylic alcohols to phenyl vinyl sulfoxide (**1a**) followed by elimination of a PhSOH unit from the adducts should generate allyl vinyl ethers **3** because several nucleophiles are known to undergo clean Michael type addition to vinylic sulfoxides[4] and even alcohol, though intramolecularly, has proven to attack β-alkoxyvinyl sulfoxide.[5] We were pleased to find that tertiary allylic alcohols smoothly added to phenyl vinyl sulfoxide (**1a**) by the action of NaH and a catalytic amount of KH to afford 2-allyloxyethyl phenyl sulfoxides **2a**. Furthermore, we have confirmed that **2a** underwent, on heating in decalin as a solvent, smooth tandem elimination and Claisen rearrangement to afford directly γ,δ-unsaturated aldehydes **4** in one-pot. In this communication, we wish to report such a new mercury-free protocol for quick access to 2-allyloxyethyl aryl sulfoxides **2** and their thermal electron reorganization leading to γ,δ-unsaturated aldehydes **4** as outlined below.

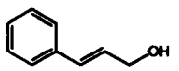
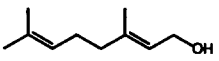
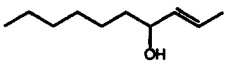
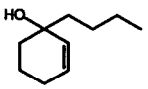
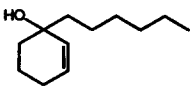
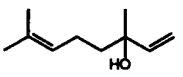
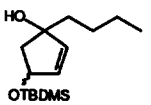
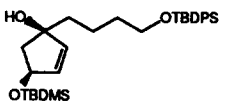


Results of the synthesis of 2-allyloxyethyl aryl sulfoxides **2** and the subsequent Claisen rearrangement are summarized in the Table. Michael-type addition of sodium alkoxides, generated from primary allylic alcohols and NaH in THF, to phenyl vinyl sulfoxide **1a** (1.2 ~ 2.0 eq) took place smoothly at room temperature to give 2-allyloxyethyl phenyl sulfoxides **2a** in good yields. In contrast, the reaction of secondary and tertiary allylic alcohols to **1a** under the same reaction conditions as above turned out to be sluggish due to a low rate of the alkoxide formation. This problem, however, was given an answer by combined use of an equimolar amount of NaH and a catalytic amount of KH. Under the conditions the reaction can be accomplished within several hours even at room temperature with high yields. It is worth noting that virtually no hydrogen evolution was observed throughout the reaction both for secondary and tertiary systems, while quite rapid hydrogen evolution was usually the case for primary system. This finding is meaningfully suggestive of a catalytic mechanism of this process.[6] The results appeared in the Table (Entries 1 and 6), where NaH was employed in a catalytic amount, clearly indicated that such a catalytic process is involved.[6] The amount of KH should be as small as possible, otherwise rapid retro Michael process was incorporated. In all the cases examined, the reaction is clean, no by-products such as polymers stemmed from the phenyl vinyl sulfoxides being detected.

The adducts thus obtained can successfully be converted into γ,δ-unsaturated aldehydes **4** when a solution of **2a** in decalin was heated at 180 °C for 2 hr under argon in the presence of $NaHCO_3$ to scavenge the releasing PhSOH. It is very important for efficient trapping of PhSOH to select proper bases which have neither nucleophilicity nor basicity toward the resultant aldehydes. In fact, an attempted thermolysis in the absence of any bases resulted in the formation of a significant amount of trash. No satisfactory result was obtained with tertiary amines except for 1,8-bis(dimethylamino)naphthalene. The best results were eventually obtained by using $NaHCO_3$.

It is expected that appending of an electron-withdrawing group on the aromatic ring of **1a** should gain access to still higher reactivity for the Michael addition. Indeed, *p*-chlorophenyl vinyl sulfoxide (**1b**) provided somewhat improved results as indicated in the Table.

Table. Synthesis of allyloxyethyl aryl sulfoxides **2** and γ,δ-unsaturated aldehydes **4** from vinyl aryl sulfoxides **1** and allylic alcohols[a]

Entry	ROH	1 (eq)	Time (hr)	NaH (eq)	KH[b]	2 (%)[c] Y=H	2 (%)[c] Y=Cl	4 (%)[c]
1		2.0	1	0.2	—	89	89	72 (Y=H) 84 (Y=Cl)
2		1.2	1	1.0	—	81	86	40 (Y=Cl)
3		3.0	3	1.0	cat.	80	88	90 (Y=H) 86 (Y=Cl)
4		3.0	3	1.0	cat.	78	79	85 (Y=H) 83 (Y=Cl)
5		3.0	3	1.0	cat.	74	87	73 (Y=H) 85 (Y=Cl)
6		3.0	3	0.2 1.0	cat. cat.	76 76	 83	79 (Y=H) 87 (Y=Cl)
7		3.0	3	1.0	cat.		82	84 (Y=Cl)
8		3.0	3	1.0	cat.	81		90 (Y=H)

a) Conducted at rt for the addition (THF) and at 180 °C (2 hr) for the elimination and rearrangement (decalin with $NaHCO_3$); b) Estimated amount ≈1 mg or less; c) For purified product by column chromatography (SiO_2) which showed satisfactory spectral data.

A typical experimental procedure is described below:

2-(1-Hexylcyclohex-2-en-1-yloxy)ethyl *p*-chlorophenyl sulfoxide (Entry 5 in the Table): To a stirred suspension of NaH (46 mg, 1.16 mmol) in THF (2 ml) was added dropwise a solution of 1-hexylcyclohex-2-en-1-ol (211 mg, 1.16 mmol) in THF (1.5 ml) at room temperature. After 30 min, a solution of *p*-chlorophenyl vinyl sulfoxide (648 mg, 3.48 mmol) in THF (1.5 ml) was added dropwise at room temperature. Then a small piece of KH was added to the mixture, and the reaction was stirred for 3 hr, being terminated by the addition of moist ether (10 ml). The mixture was washed (water), dried ($MgSO_4$), and

addition of moist ether (10 ml). The mixture was washed (water), dried ($MgSO_4$), and concentrated to give an oil. The crude oil was purified by column chromatography (SiO_2) to afford the adduct as an oil (374 mg, 87% yield).

Claisen rearrangement of the allyl vinyl ether from 2-(1-butylcyclohex-2-en-1-yloxy)ethyl *p*-chlorophenyl sulfoxide (Entry 5 in the Table): The adduct (324 mg, 0.88 mmol) was mixed with $NaHCO_3$ (38.6 equiv) in decalin (3 ml), and the mixture was heated at 180 °C for 2 hr. Ether (40 ml) was added to the mixture and the solution was washed with water and dried ($MgSO_4$). The yellow oil, obtained after evaporation of the solvent, was purified by column chromatography (SiO_2) to give (3-butylcyclohex-2-enyl)acetaldehyde (155 mg, 85% yield).

In conclusion, we have successfully developed the mercury-free preparative method for allylic vinyl ethers, which can be applied to diverse allylic alcohols including otherwise impossible tertiary systems. Synthetic applications of this method are under investigation.

References

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3) The reaction of allyl alcohols with phenyl trifluoroethyl sulfoxide via in situ formation of difluorovinyl phenyl sulfoxide has been reported. Releasing of HF, in this case, led to allyl fluorovinyl ether, which underwent Claisen rearrangement: Nakai, T.; Tanaka, T.; Ogasawara, K.; Ishikawa, N. *Chem. Lett.* **1981**, 1289.

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6) Description of the mechanistic detail will be presented elsewhere.

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