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Trapping of Payne rearrangement intermediates with arylselenide anions

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ABSTRACT

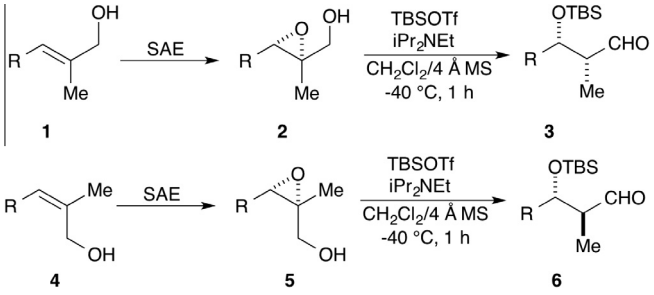
The intermediate epoxy alcohols prepared via a Payne rearrangement can be trapped with arylselenide anions, giving mixtures of ring-opened products. The 1-arylseleno-2,3-diols are generally favored over the 3-arylseleno-1,2-diols in this process although the reaction of trisubstituted epoxyalcohols, for example, **17**, differs from those of disubstituted epoxyalcohols, for example, **21**.

Several years ago we reported the rearrangement of epoxy alcohols and their silyl ethers using silyl triflates to produce silyl-protected aldol products in a process we termed the 'non-aldol aldol'.[1] Although the epoxy alcohols **2** prepared using a Sharpless asymmetric epoxidation of the *E* 2-methyl allylic alcohols **1** gave very good yields of the aldol products **3**, the reaction of the epoxides **5** derived from the corresponding *Z* allylic alcohols **4** could be problematic due presumably to steric hindrance to the desired rearrangement, although conditions were found to produce the anti aldol products **6** (Scheme 1).[2] We wondered whether a longer sequence involving a double inversion process might allow us to obtain the anti aldol products **10** from the *E* epoxy alcohols **2** (Scheme 2). This would involve the trapping of the Payne rearrangement[3] equilibrium of **2** and **7** with a strong nucleophile to give **8**, followed by selective protection of the secondary alcohol and cyclization to the terminal epoxide **9** and then final Yamamoto rearrangement[4] to give the anti aldol product **10**. We report here our results of the trapping of the Payne rearrangement intermediates using aryl selenide anions.

In a beautiful approach to the synthesis of the alditols,[5] Sharpless and Masamune reported the interception of one of the intermediates of the Payne rearrangement with thiolates to give selectively the 1-thiophenyl-2,3-diols (Scheme 3). Thus treatment of the epoxy alcohol **11** with thiophenol and aq sodium hydroxide in dioxane afforded the product of selective opening of the intermediate rearranged epoxy alcohol **12** at the primary center to give predominately the product **13**. Later Boeckman showed that this same process occurred with the methyl substituted epoxy alcohol **15** to give the diol **16** in an elegant synthesis of (−)-kromycin.[6] We decided to study the analogous rearrangement using arylselenide anions instead of the phenylthiolates. Herein we report the results of that investigation.

The epoxy alcohols were all prepared by an application of Sharpless asymmetric epoxidation[7] of the readily available *E*- and *Z*-allylic alcohols. We decided to test one substrate in order to find the best conditions for the rearrangement-trapping process (Scheme 4) and therefore prepared the known epoxy alcohol **17**.[1a]

Since the preference for opening the terminal epoxide **18** over the internal epoxide **17** is due to steric hindrance, we decided to use a very sterically hindered arylselenide. Thus the known



Scheme 1. Non-aldol aldol reaction to give **3** and **6**.

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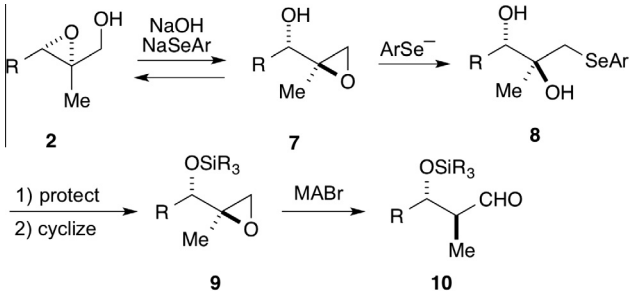
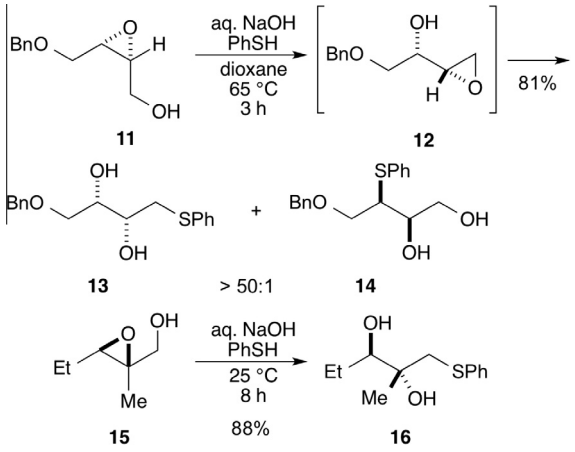
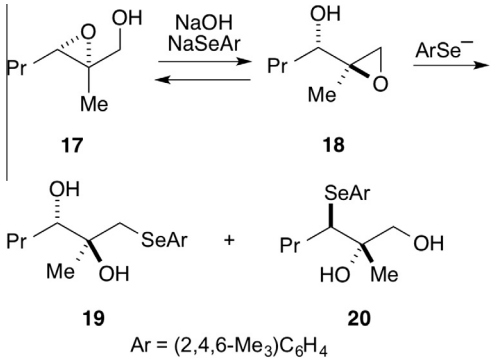


Scheme 2. Alternative route for anti aldol products **10**.



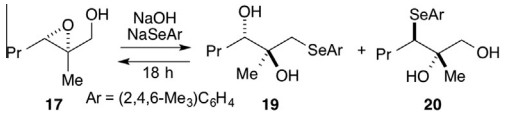
Scheme 3. Selective trapping of the Payne intermediate **12**.

bis(2,4,6-trimethylphenyl)diselenide (dimesityl diselenide)[8] was reduced with sodium borohydride to give the mesitylselenide anion. To a solution of the epoxy alcohol **17** in ethanol was added over 2 h a solution of the sodium mesitylselenide and 1 M (or 0.5 M) NaOH. All of the reactions were stirred for 18 h. The results (Table 1) showed that the temperature had a significant effect, namely higher temperatures generally gave more of the desired 1-seleno-2,3-diol **19** than the product of direct opening, the 3-seleno-1,2-diol **20** (entries a–d).[9] Heating **17** with the selenide in ethanol at 85 °C (reflux) afforded the desired product in 48% yield along with 34% yield of the undesired product (entry d). Interestingly, adding all of the selenide and base at once seemed to improve the yield of the desired product (entry e vs entry b). However, higher temperatures in other solvents, for example, 100 °C in isopropanol or aq *tert*-butanol, gave much poorer results (entries f and g). The ratio of the desired to undesired product was



Scheme 4. Formation of the arylseleno diols.

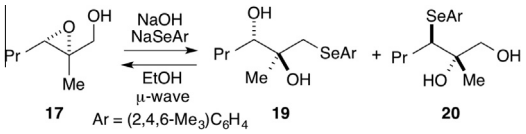
Table 1
Treatment of **17** with NaSeAr to give **19** and **20**



Entry	Solvent	Temp (°C)	**19** (%)	**20** (%)	Overall yield (%)
a	EtOH	0	13	45	58
b	EtOH	22	31	53	84
c	EtOH	45	40	23	63
d	EtOH	85	48	34	82
e[a]	EtOH	22	44	35	79
f[b]	*i*PrOH	100	30	13	43
g[b]	aq *t*BuOH	100	10	10	20

[a] Added all at once.
[b] 0.5 M NaOH was used.

Table 2
Reaction of **17** under microwave conditions to give compounds **19** and **20**

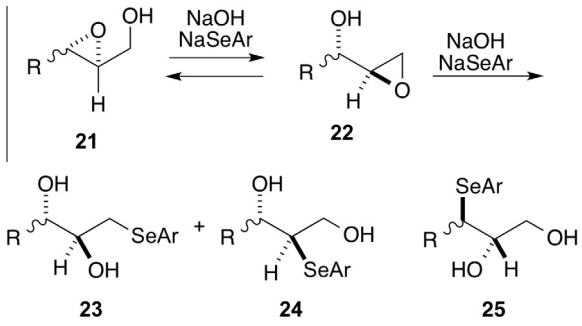


Entry	Time (h)	Temp (°C)	**19** (%)	**20** (%)	Overall yield (%)
a	48	100	51	10	61
b	12	100	46	23	69
c	48	85	41	0	41
d	12	85	60	17	77
e[a]	60	80	56	0	56

[a] Not microwave; sealed tube.

best at 45 °C (1.7:1) but the overall yield was lower than that at 85 °C where the ratio was 1.4:1 (entries c and d).

We next investigated the use of microwave heating for this process since some non-thermal effects have been observed especially in reactions of polar substrates.[10] Thus the epoxy alcohol **17** was treated with the sodium mesitylselenide and 1 M NaOH in ethanol at 22 °C. The mixture was then placed in an industrial microwave oven and heated to the indicated temperatures for the time shown. The results (Table 2) indicated that these microwave conditions were favorable for the formation of the desired product **19** in preference to the undesired product **20**. At all temperatures, shorter reaction times were better, presumably due to decomposition of the products on prolonged heating with base. Thus at 100 °C, the shorter time of 12 h was somewhat better than 48 h, although the ratio was better at longer times (entries a and b). And at 85 °C, heating for 12 h afforded 60% of the desired product **19** along



Scheme 5. Rearrangement-trapping of the disubstituted epoxy alcohols **21** to give the three products **23**–**25**.