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Trapping of Payne rearrangement intermediates with arylselenide anions

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A B S T R A C T

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’. 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). 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 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 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, 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. 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 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. 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...
bis(2,4,6-trimethylphenyl)diselenide (dimethyl diselenide) was reduced with sodium borohydride to give the mesitylselenide anion. To a solution of the epoxy alcohol 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 than the product of direct opening, the 3-seleno-1,2-diol (entries a–d).

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 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. 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...
with 17% of the undesired 20, while heating for 48 h gave only the desired product but in the lower yield of 41% (entries c and d). Finally we also investigated the use of heating in a sealed tube for an extended period. Thus heating an ethanolic solution of 17 at 80 °C in a sealed tube for 60 h gave only the desired product 19 in an isolated yield of 56%. The undesired product 20 seems to be selectively destroyed on prolonged heating. Therefore the best method for preparing the desired products was heating at 80–85 °C in ethanol, either via microwave or thermal heating.

Using a series of disubstituted epoxides, we then looked at the substrate scope of the rearrangement-trapping process. In these substrates, three different products can be obtained, from opening at either end of the original epoxide 21, giving 24 and 25, or the terminal epoxide 22 giving 23 (Scheme 5). All of the epoxy alcohol substrates, 21a–g, were prepared by known routes5 using the Sharpless asymmetric epoxidation. Each was mixed with the sodium mesitylselenide and 1 M NaOH in ethanol and heated at 85 °C for 18 h. The results (Table 3) indicate firstly that the overall yields for these substrates were excellent, generally greater than 90%. Secondly, for these substrates not having the 2-methyl substituent, significant opening at C2 occurred to generate the 2-seleno-1,3-diol 24.11 Thus the relatively unhindered substrates gave significant amounts of the 2-seleno products (entries a–d) with relatively similar amounts of the 1-seleno and 3-seleno products, 23 and 25, respectively. When the attack of the hindered arylselenide anion at C-3 is made more difficult, due to the steric interaction of the acetonides, then no opening at C-3 is observed but only a mixture of the C-1 and C-2 products, 23 and 24. In these latter three cases (entries e–g), reasonable yields of the 1-seleno product 23 could be isolated.

Table 3
Reactions of disubstituted epoxy alcohols

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Yield of 1-seleno-2,3-diol 23 (%)</th>
<th>Yield of 2-seleno-1,3-diol 24 (%)</th>
<th>Yield of 3-seleno-1,2-diol 25 (%)</th>
<th>Overall yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td></td>
<td>39</td>
<td>0</td>
<td>46</td>
<td>85</td>
</tr>
<tr>
<td>b</td>
<td></td>
<td>24</td>
<td>51</td>
<td>24</td>
<td>99</td>
</tr>
<tr>
<td>c</td>
<td></td>
<td>42</td>
<td>27</td>
<td>30</td>
<td>99</td>
</tr>
<tr>
<td>d</td>
<td></td>
<td>28</td>
<td>29</td>
<td>36</td>
<td>93</td>
</tr>
<tr>
<td>e</td>
<td></td>
<td>65</td>
<td>29</td>
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<td>94</td>
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<tr>
<td>f</td>
<td></td>
<td>53</td>
<td>40</td>
<td>0</td>
<td>93</td>
</tr>
<tr>
<td>g</td>
<td></td>
<td>52</td>
<td>24</td>
<td>0</td>
<td>76</td>
</tr>
</tbody>
</table>

Since heating the mixture of the epoxy alcohols and the arylselenide anion in ethanol for longer periods of time seemed to give more of the desired 1-seleno product with respect to the 3-seleno product (Table 2), we wondered if the formation of the selenodiols might well be reversible under these conditions. The product 20 formed by opening the starting epoxyalcohol 17 at C-3 might well be revert back to 17 via loss of the mesitylselenide anion before being converted via 18 into the desired product 19 (Scheme 6). Therefore we treated the isolated, pure 3-seleno-1,2-diol 20 with sodium mesitylselenide and 1 M sodium hydroxide in ethanol at 85 °C for 18 h and isolated a mixture of the two products, the starting material in 74% yield and the rearranged product 19 in 23% isolated yield (Scheme 7). Thus the seleno diol 20 must lose the mesitylselenide anion and revert back to the epoxy 17, rearrange via Payne rearrangement to the isomeric epoxide 18, and
then be opened at the terminal end of the epoxide 18 with the aryl-selenide anion to give 19. This implies that the formation of the products may be partially controlled by thermodynamic effects and not merely kinetic effects.

In conclusion, we have developed a useful method for the conversion of 1,2-epoxy alcohols to the corresponding 1-seleno-2,3-diols using the hindered mesitylselenide anion under basic conditions in refluxing ethanol. The use of these compounds is under investigation and will be reported in due course.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2014.11.103.

References and notes


2. Jung, M. E.; Lee, W. S.; Sun, D. Org. Lett. 1999, 1, 307–309. The yields of the anti aldol products in these hindered cases were lower due to competing elimination to give the allylic bis(silyl ethers).


9. The structures of the 1-seleno-2,3-diols 19 and the 3-seleno-1,2-diol 20 were determined by high field proton NMR experiments, in which the chemical shift of the easily identifiable methylene group was at either lower field (α to oxygen) or at higher field (α to selenium).


11. The structures of the 2-seleno-1,3-diols 24 and the 3-seleno-1,2-diols, 25 were determined by high field proton NMR experiments, especially of the acetylated products, by careful matching of coupling constants and chemical shifts of the lower field protons, along with NOESY and COSY spectra.

Scheme 7. Rearrangement-trapping of the disubstituted epoxy alcohols 21 to give the three products 23–25.