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A SYNTHESIS OF ALLYLIC ALCOHOLS FROM β,γ-EPOXYSULFONES

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The Evans-Mislow synthesis of allylic alcohols[1] entails the alkylation of an allylic sulfoxide anion followed by a [2,3]-sigmatropic rearrangement to an intermediate sulfenate ester which can be trapped by thiophilic reagents to give an allylic alcohol. The elegance of this procedure is partially compromised by the mediocre yields in the sulfoxide alkylation[2] and the lack of regiospecificity in the alkylation[3].

An alternative to the Evans-Mislow procedure is presented below which exploits the efficient and regiospecific alkylation of allylic sulfones 1 and the reductive elimination of the derived diastereomeric epoxysulfones 3 to give allylic alcohols in moderate to good overall yields. The regiochemical advantages of the sulfone-based sequence are exemplified by comparing the alkylation **1a** → **2a**(n-hexyl bromide, 96% yield, exclusively α) with the corresponding sulfoxide (n-hexyl iodide, 42% yield, $\alpha:\gamma = 2{\cdot}5$)[2].

A disadvantage of the new method is that the reductive cleavage of the epoxysulfones 3a,b is not stereospecific but gives E,Z-mixtures of tri-substituted allylic alcohols 4a,b[4]. This is not due to stereospecific reductive eliminations since the crystalline major diastereomer (m.p. 58-60°; 70% of the mixture) of the epoxysulfones 3a and the minor oily diastereomer (30% of the mixture) afforded on reduction the allylic alcohols 4a in 73% yield (E:Z::5:1) and 62% yield (E:Z::2:1) respectively.

The transformations reported herein represent a potentially useful extension of recent methods which deploy the reductive elimination of β-substituted sulfones for the synthesis of olefins[5-13] and acetylenes[14-15].

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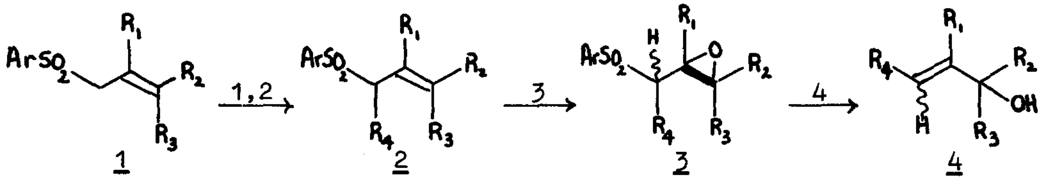

	R_1	R_2	R_3	Yield 7	Yield 9[5]
a	Me	H	H	93%	70% (E:Z::7:3)
b	H	Me	H	96%	62% (E:Z::4:1)
c	H	Me	Me	97%	89% (E only)

Ar = p-Tolyl, R_4 = n-hexyl

1) n-Buli; 2) 1·25 eq n-hexyl bromide, 1·25 eq HMPA, 0°; 3) 2 eq m-$ClC_6H_4CO_3H$; 4) 4 eq 5·6% Na(Hg)/THF-MeOH (3:1), -20°; 5) E/Z ratios determined by nmr and vpc.

References and Notes

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