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Butyllithium-Induced Syn β-Elimination of 2-Arylalkyl p-Toluenesulfonates

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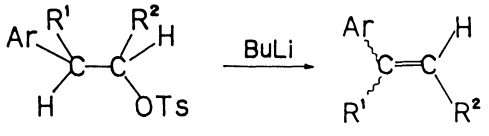
Erythro- and threo-1-methyl-2-phenylpropyl tosylates regiospecifically undergo syn β-elimination on treatment with butyllithium in THF with 88 and 96% d. e. respectively.

Base-induced β-elimination reactions of 2-arylalkyl tosylates proceed exclusively via the anti route.[1] We show here butyllithium to effect syn elimination from 2-arylalkyl tosylates **1a-1c.**

When butyllithium (1.1 equiv.) was added to a solution of 2-phenylethyl tosylate (**1a**, 3 mmol) in THF (10 cm^3) at -78 °C and the mixture was stirred for 2 h at room temperature, there was obtained styrene (**2a**) in 45% yield besides the unchanged tosylate (37%). The formation of styrene does not arise from a normal E2 reaction. Addition of chlorotrimethylsilane at -78 °C prior to warming resulted in the formation of an o-silylated ester **3** instead of styrene, indicating an elimination reaction from an o-lithiated intermediate **5.**[2] Noteworthy is the stereochemistry. Erythro-1-methyl-2-phenylpropyl tosylate (**1b**) exclusively gave (Z)-2-phenyl-2-butene (**2b**), while the threo-isomer gave (E)-**2b** on treatment with n-BuLi, the products of syn elimination in both cases. The results are given in Table 1.

Relative rates of the intramolecular elimination from **5a** and **5b** were determined by competition experiments as follows: k(erythro-**5b**)/k(**5a**)=0.24 and k(threo-**5b**)/k(erythro-**5b**)=2.0. Acidity of β-hydrogens and steric requirements of the syn-oriented transition state **5** are probably respon-



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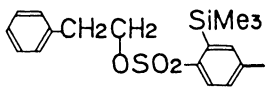
a) Ar=C6H5, R¹=R²=H
b) Ar=C6H5, R¹=R²=CH3
c) Ar=m-ClC6H4, R¹=H, R²=C6H5CH2
d) Ar=C6H5, R¹=H, R²=m-ClC6H4CH2



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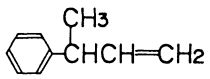

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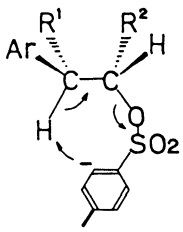

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Table 1. n-BuLi-Induced Elimination Reactions of 2-Arylalkyl Tosylates

Tosylate	Conditions	Products [ratio]	Yield/%[a]
1a	n-BuLi/THF, 2 h[b]	**2a**	45, 71[c]
	n-BuLi/THF, Me_3SiCl[d]	**3**	72, 92[c]
threo-**1b**	n-BuLi/THF, 5 h[b]	(E)-**2b** + (Z)-**2b** [98:2]	93
	EtONa/EtOH	(E)-**2b** + (Z)-**2b** + **4** [3:84:13][e]	
erythro-**1b**	n-BuLi/THF, 5 h[b]	(E)-**2b** + (Z)-**2b** [6:94]	58, 87[c]
	EtONa/EtOH	(E)-**2b** + **4** [91:9][e]	
1c	n-BuLi/THF, 1 h[b]	(E)-**2c** + (Z)-**2c** [88:22]	80, 92[c]
	t-BuOK/t-BuOH[f]	**2c**[g] + **2d**[g] [62:38]	72
	t-BuOK/DMSO[h]	**2c**[g] + **2d**[g] [34:66]	i)

a) Isolated yield. b) After addition of BuLi at -78 °C, the mixture was allowed to stand at room temperature. c) Corrected for the unchanged **1**. d) At -78 °C. e) Data taken from Ref. 1a. f) Reflux, 4 h. g) (E) exclusively. h) At room temperature for 1 h. i) Not determined.

sible for these rate ratios. Another characteristic feature of the present elimination is the regioselectivity. While **1b** gives a mixture of **2b** and its regioisomer **4** under E2 conditions, it gave **2b** regiospecifically when treated with n-BuLi. A more striking result is the elimination reaction of 2-(m-chlorophenyl)-1-benzylethyl tosylate (**1c**). Whereas E2 conditions hardly discriminate the two different types of β-hydrogens of **1c** resulting in the formation of 1-(m-chlorophenyl)-3-phenyl-1-propene (**2c**) and its regioisomer **2d** in comparable ratios, n-BuLi effected a practically regiospecific elimination to **2c**. Clearly, the intramolecular elimination of **5** is very susceptible to the acidity of β-hydrogens to be deprotonated.

Intramolecular bases may not be limited to the o-lithiated tosyloxy leaving group. We have found that 2-phenylalkyl acetates also underwent a syn elimination when treated with 2.2 equiv. LDA presumably via an enolate dianion.[3]

References

1) a) W.-B. Chiao and W. H. Sounders, Jr., J. Org. Chem., 45, 1319 (1980); b) D. J. Cram, J. Am. Chem. Soc., 74, 2149 (1952).
2) J. N. Bonfiglio, J. Org. Chem., 51, 2833 (1986).
3) Treatment with 1.1 equiv. LDA did not lead to the formation of alkenes but gave the corresponding alcohols. This would suggest that the enolate anion decomposes via an acyl-O bond cleavage more rapidly than it undergoes an intramolecular elimination.

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