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Diastereoselective Reaction of Aldehydes with 3-Bromocyclohexene and Tin

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DIASTEREOSELECTIVE REACTION OF ALDEHYDES WITH 3-BROMOCYCLOHEXENE AND TIN

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Abstract: *The reaction of 3-bromocyclohexene and powdered tin with aromatic aldehydes and an alkynal provides excellent erythro-selective products, while the corresponding reactions with aliphatic aldehydes proceed with moderate erythro-selectivity.*

Allylation of aldehydes with allylic tin compounds can afford homoallylic alcohols with impressive regio- and diastereo- selectivity.[1] Recently, the stereochemistry of cycloalkenylation of aldehydes using organotin reagents in $BF_3 \cdot Et_2O$-mediated[2] or in $BuSnCl_3$-mediated[4] proceeses or under high pressure (9 Kbr)[3] has been studied. In some cases the reaction of 2-cyclohexenyltin reagents with benzaldehyde can provide good *erythro*-selectivity, but highly toxic organotin reagents were used. In this paper, we wish to report a rather simple and

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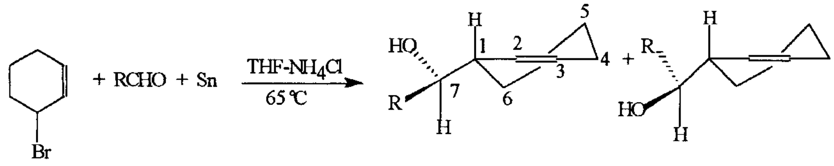

1 **2** **3a** *erythro* **3b** *threo*

Scheme 1

direct but highly *erythro*-selective 2-cyclohexenylation of aromatic aldehydes and an alkynal using powdered tin and 3-bromocyclohexene(**Scheme 1**).

The results are summarized in Table 1. The stereochemistry of **3** was determined by observation of ^{1}H NMR data and comparison with the same or similar compounds.[2,5] It was found that when 3-bromocyclohexene and powdered tin reacted with aromatic aldehydes or the alkynal, excellent *erythro*-selectivity was obtained. However, the reactions with aliphatic aldehydes go with only moderate *eyrthro*-selectivity. Such diastereoselectivity can be rationalized by the transition states proposed by Yamamura.[4]

Experimental

A general experimental procedure is as follows: A suspension of 3-bromocyclohexene[6](1.21 g, 7.5 mmol), powdered tin[7] (0.90 g, 7.5 mmol), benzaldehyde (0.53 g, 5.0 mmol), and THF-NH$_4$Cl(aq) (5:1, 10 mL) was stirred for 24 h at 65°C (monitored by TLC). After removal of the solvent, saturated brine(5.0 mL) was added; the mixture was extracted with ether (3 x 20 mL), the

Table 1. The reaction of 3-bromocyclohexene and powdered tin with aldehydes

Entry	RCHO R=	Yield of product (%)[a]	ratio of **3a**:**3b**[b]
1	C_6H_5	80.0	>99:1[c]
2	$4\text{-}ClC_6H_4$	85.0	>99:1[c]
3	$3\text{-}C_6H_5OC_6H_4$	90.5	>99:1[c]
4	$CH_3(CH_2)_4C{\equiv}C$	60.0	>99:1[c]
5	$n\text{-}C_3H_7$	71.0	62:38
6	$n\text{-}C_4H_9$	79.0	64:36
7	$n\text{-}C_5H_{11}$	75.0	65:35
8[d]	$(CH_3)_2C{=}CH(CH_2)_2CH(CH_3)CH_2$	62.5	60:40

a: isolated yield based on corresponding aldehyde; b: ratio was determined by ^1H NMR spectra; c: threo-isomer was not detected by ^1H NMR spectra. d: citral

combined extracts were dried over anhydrous sodium sulfate, then the ether was evaporated and the residue was purified by column chromatography on silica gel, using petroleum ether and ethyl acetate (10:1) as the eluent.

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8. The ^{1}H NMR spectrum was taken on a Bruker MSL-300 (300 MHz, Fourier Transform Mode Spectrometer). Typical analysis data for product 1-(1'-hydroxybenzyl-*m*-phenoxy)cyclohex-2-ene are: δ_H (CDCl3): 1.43-1.55 (2H, m, 2 × H^6), 1.63-1.76(2H, m, 2 × H^5), 1.94-1.97(2H, m, 2 × H^4), 2.02(1H, br, OH), 2.45(1H, m, H^1), 4.55(1H, d, H^7, J_{H7-H1} = 6.3 *Hz*), 5.40(1H, m, H^2), 5.81(1H, m, H^3), 6.88-7.34(9H, m, C_6H_4-O-C_6H_5) ppm. IR υ_{max}: 3450(s, OH), 1650(m, C=C) cm^{-1}. MS *m/z*(%): 281(M$^+$1, 3.76), 263(M-OH, 100.0), 199(M-C_6H_9, 72.9), 171(M-C_6H_9CO, 78), 81(C_6H_9, 34.7). $C_{19}H_{20}O_2$ Calc.: C, 81.39; H, 7.19. Found: C, 80.95; H, 7.36.

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