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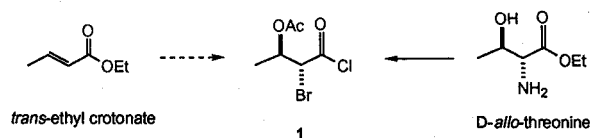
A New Route to a Key Chiral Intermediate of Thienamycin from *trans*-Ethyl Crotonate

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Thienamycin,¹ a β -lactam antibiotic exhibiting broad antibiotic activity, and its derivatives are continuing targets for research and development in the area of antibiotics.² Among various intermediates^{2b,c} to those compounds, acid chloride **1** is unique in that the corresponding amides afford the β -lactam ring, azetidinones, *via* a complete intramolecular S_N2 type cyclization.³ The intermediate **1** has been prepared as a chiral form from *D*-*allo*-threonine⁴ or as a racemic form from *trans*-crotonic acid.³ Considering the high cost of nonracemic threonine, we counted that any route to chiral intermediate **1** from cheap crotonates would be quite compatible.

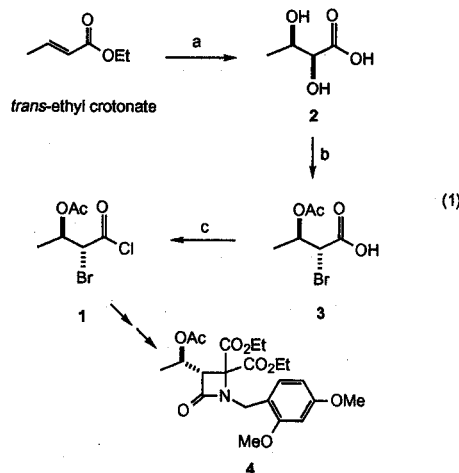


Scheme 1.

In this brief communication, we describe a concise route to **1** from *trans*-ethyl crotonate employing asymmetric dihydroxylation (ADH).⁵ Although structural transformations after ADH reactions from α,β -unsaturated esters to acetoxy bromo esters have been reported,⁶ to our best knowledge, any route to **1** or to acetoxy bromo acyl chloride derivatives has not been developed. We followed a known procedure⁶ using (DHQD)₂PHAL⁷ to obtain *threo*-2,3-dihydroxy ester in 94% yield. And hydrolysis of the ester using LiOH in MeOH afforded the corresponding acid **2**⁸ quantitatively. The dihydroxy acid **2** was transformed with HBr in acetic acid to provide *erythro*- β -acetoxy- α -bromo acid **3**⁸ in 91% yield. Finally, the desired acyl chloride **1** was readily prepared by treating **3** with SOCl₂ in methylene chloride in a quantitative yield.

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With no necessity of purification, the four step sequence from the crotonate afforded the intermediate **1** in good yields. This reaction sequence would be applicable in general for the preparation of analogue acid chlorides. And the intermediate **1** was converted to a known azetidinone **4** for comparison using dimethoxybenzylaminomalonate.⁹ The spectral data of **4** (¹H NMR, ¹³C NMR) matched well with those in the literature,⁹ though the optical purity is lower ($[\alpha]_D^{24} + 30.9^\circ$ ($c=2.0$, EtOH), lit.⁹ $[\alpha]_D^{24} + 39.5^\circ$ ($c=2.03$, EtOH)).



Reagents: a. (DHQD)₂PHAL, K₂OsO₂(OH)₄, NMO, *t*-BuOH; LiOH, MeOH
b. HBr, AcOH, 45°C c. SO₂Cl₂, CH₂Cl₂

In conclusion, this concise route employing practical procedures suggests a compatible pathway to the key intermediate, and the optimization for optical purity is left as further work.

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8. **2**: ^1H NMR (300 MHz CD_3OD): δ 1.26 (d, $J=5.7$ Hz, 3H); 4.12 (bs, 2H).
3: ^1H NMR (300 MHz CDCl_3): δ 1.45 (d, $J=6.0$ Hz, 3H); 2.08 (s, 3H); 4.39 (d, $J=7.2$ Hz, 1H); 5.28 (m, 1H); 11.04 (bs, 1H).
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Catalytic Dehydropolymerization of 3-Aryl-1-silabutanes by $\text{Cr}(\text{CO})_6$

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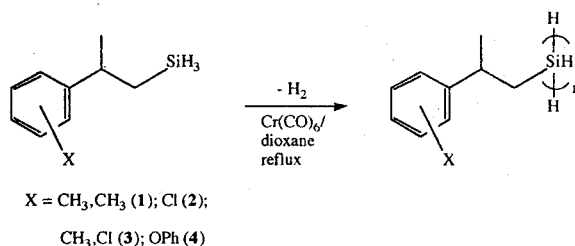
A great deal of attention has recently been focused on the synthesis of polysilanes with unusual optical and electronic properties due to σ -conjugation along the silicon backbone. Polysilanes have been used for many special applications such as ceramic precursors, third-order NLO materials, deep-UV photoresists, photoconductors, and photoinitiators.¹ The conventional synthetic method to currently get high-molecular-weight polysilanes has been the Wurtz coupling reaction of dichlorosilanes using alkali metals, which are intolerant of some functional groups, lack of reproducibility, and have some limitations for controlling stereochemistry and molecular weight distributions.

Harrod's recent discovery of group 4 metallocene-catalyzed dehydropolymerization led to great progress in poly(organo-silane) synthesis.² A major handicap of the metallocene-catalyzed dehydrocoupling method is the production of low-molecular-weight polysilanes which affects mechanical and optical properties.^{2,3} Intensive efforts have been made to increase the molecular weight of the polysilanes by a broad screening of various early transition metallocenes,⁴ by studies on the reaction intermediates and mechanism,⁵ and by employing versatile silanes.^{6,7}

Harrod *et al.* unsuccessfully attempted the catalytic dehydropolymerization of phenylsilane by group VI metallocenes.^{4a} Tilley *et al.* described the preparation and dehydropolymerization of chromium tricarbonyl derivative of benzylsilane by using group IV metallocene catalyst.⁸ We reported earlier the dehydropolymerization of 3-aryl-1-silabutanes catalyzed by group IV metallocene $\text{Cp}_2\text{MCl}_2/\text{Red-Al}$.⁹ To our knowledge, group VI metal hexacarbonyl complexes have never been used for the dehydropolymerization of silanes. Although Cp_2MMe_2 ($\text{M}=\text{Ti}, \text{Zr}$),² $\text{Cp}_2\text{Zr}[\text{Si}(\text{SiMe}_3)_3]\text{Me}$,^{3a-d} and $\text{Cp}_2\text{ZrCl}_2/n\text{-BuLi}$ ¹⁰ are known to be the active catalysts for the dehydropolymerization of primary silanes and $\text{CpCp}^*\text{Zr}[\text{Si}(\text{SiMe}_3)_3]\text{Me}$ and $(\text{CpCp}^*\text{ZrH}_2)_2$ were the most active catalyst previously examined,^{3a-d} we wanted to employ a novel catalyst, $\text{Cr}(\text{CO})_6$ to compare with $\text{Cp}_2\text{MCl}_2/\text{Red-Al}$ ($\text{M}=\text{Ti}, \text{Hf}$),⁹ which

was recently found to give predominantly linear, higher molecular weight of polysilanes than for any other catalyst system.¹¹ In this communication we wish to report the catalytic dehydropolymerization of 3-aryl-1-silabutanes by group VI transition metal hexacarbonyl complex $\text{Cr}(\text{CO})_6$.

In a typical experiment, dioxane (4 mL) was added to a Schlenk flask charged with $\text{Cr}(\text{CO})_6$ (62 mg, 0.28 mmol) and 3-(2,5-dimethylphenyl)-1-silabutane **1** (1.0 g, 5.6 mmol). The reaction mixture was heated at dioxane-refluxing temperature for 3 days. The green viscous solution was then passed rapidly through a silica gel column (70-230 mesh, 20 cm \times 2 cm). The column was rinsed with 200 mL of diethyl ether.



The removal of volatiles at reduced pressure yielded 0.88 g (88% yield) of off-white tacky product.¹² Similarly, the dehydropolymerization of the other 3-aryl-1-silabutanes such as 3-(chlorophenyl)-1-silabutane **2**, 3-(chloro-*p*-tolyl)-1-silabutane **3**, and 3-(phenoxyphenyl)-1-silabutane **4** was also carried out to give the corresponding polysilanes as off-white tacky products.¹³

The results are summarized in Table 1.

Dehydropolymerization of **1-4** catalyzed by $\text{Cr}(\text{CO})_6$ was not occurred at room temperature probably due to the low solubility of $\text{Cr}(\text{CO})_6$ in dioxane, but the reaction medium became rapidly viscous upon being heated at dioxane-refluxing temperature. All of the resulting polysilanes were soluble in most organic solvents. Compared with dehydropolymerization of **1-4** catalyzed by group IV metallocenes, the polymerization yields and the spectroscopic data of polysilanes produced with $\text{Cr}(\text{CO})_6$ were almost same.¹¹⁻¹³ This fact implies that the polysilanes produced by the dehydropolymerization of **1-4** with group IV metallocenes and $\text{Cr}(\text{CO})_6$ must have the similar structures. However, the weight average molecular weights of the polysilanes produced with $\text{Cr}(\text{CO})_6$ were much higher (by up to five times) than those produced with group IV metallocenes.

Table 1. GPC Characterization of Polymerization of Monomer Silanes with $\text{Cr}(\text{CO})_6$ ^a

Monomer	Yield (%)	mol wt ^b		
		\bar{M}_w	\bar{M}_n	PDI ^c
1	88	5810	630	9.2
2	80	4150	1340	3.1
3	90	2140	1010	2.1
4	92	1110	280	4.0

^a $[\text{Cr}]/[\text{Si}]=0.05$; refluxing in dioxane for 3 days. ^b Measured with GPC in toluene (*vs* polystyrene). ^c Polydispersity index, \bar{M}_w/\bar{M}_n .