Tetrahedron Letters,Vol.30,No.42,pp 5745-5746,1989 0040-4039/89 $3.00 + .00
Printed in Great Britain Pergamon Press plc

Stereoselectivity in the Reaction of Acyliron Complexes with Allylstannanes

James W. Herndon* and Chao Wu

Department of Chemistry and Biochemistry

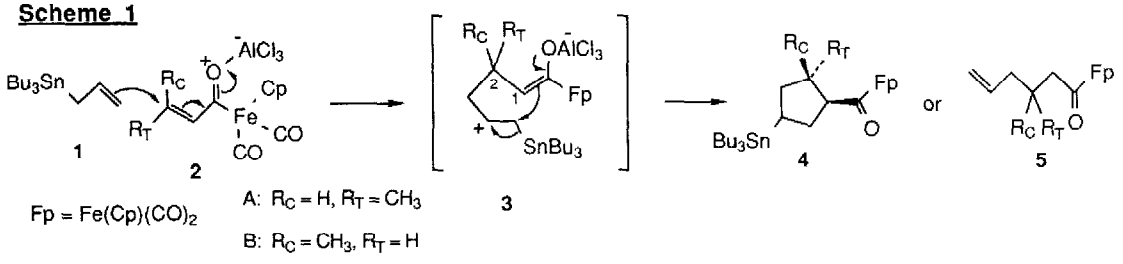
University of Maryland

College Park, Maryland 20742

Summary: The reaction of allylstannanes with α,β-unsaturated acyliron complexes and $AlCl_3$ to give five-membered rings was found to be highly stereoselective. Reaction of the trans-crotonyliron complex with allyltributyltin provided exclusively the adduct where the acyliron and methyl groups are trans. Reaction of the cis isomer provided the corresponding cis cyclopentane.

Recently, we reported that α,β-unsaturated acyliron complexes react with allyltins and $AlCl_3$ to produce predominately cyclopentane derivatives[1] (Scheme 1). In some cases, predominately the open-chain product was obtained. These reactions were found to be highly stereoselective, producing only a single diastereomer in all cases. Since neither allyltins nor α,β-unsaturated acylirons are conveniently available in stereochemically pure form[2], the dependence of the reaction outcome on the stereochemical configuration of the starting alkenes was not determined in the preliminary communication. Herein we report how the double bond configuration of the starting α,β-unsaturated acyliron complex affects the outcome of the reaction.

Scheme 1

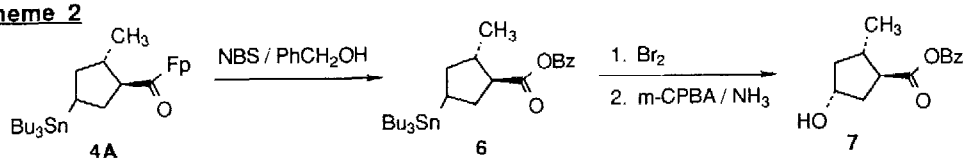


A synthetic route to the cis crotonyliron complex **2B** has not been reported. In the one attempt to prepare this compound[3], complete isomerization to the trans complex occurred. The corresponding triphenylphosphine-substituted analog of this complex has been prepared[4], however this complex was not reactive to allyltins and $AlCl_3$. If the crude reaction mixture was purified by fractional distillation (b.p. 35 - 50°C; 0.01 mmHg), then a mixture of the cis and trans isomers was obtained, which were easily separable by flash column chromatography on silica gel.

Reaction of the trans-crotonyliron complex (**2A**) with allyltributyltin and $AlCl_3$ led to the formation of a single stereoisomer assigned as **4A**[5] in 41% yield. Reaction of cis complex **2B** with $AlCl_3$ under the same conditions (25°C, 3 h) led to a mixture of a new diastereomer assigned as **4B**[5] along with compound **4A**, accompanied by a trace (< 5%) of the open-chain product **5A**. $AlCl_3$ did not catalyze the interconversion of **4A** and **4B**. These results are consistent with a stepwise mechanism for the addition of allylstannanes to α,β-unsaturated acyliron complexes (Scheme 1). However, $AlCl_3$ catalyzed the complete isomerization of cis

complex **2B** to trans complex **2A** in a period of 2 h at 0°C. When complex **2B** was treated with $AlCl_3$ for 1 min before allyltributyltin was added, and reaction was stopped long before completion (10 min at 0°C), only **4B** was obtained in 23% yield. If this is indeed the mechanism of the reaction, the ring closure step must occur much faster than any rotation about the C1 - C2 bond in zwitterionic intermediate **3**. In the extreme, this reaction may be looked at as a concerted reaction. Similar results in a related system, the reaction of allenylsilanes with enones[6], have also been observed. Compound **4A** was demetallated according to the sequence of reactions outlined in Scheme 2. Reaction of the ester **6** with bromine, then basic m-CPBA led to alcohol **7** in 65% yield, having the indicated stereochemistry[7].

Scheme 2



In summary, the stereochemistry about the alkene in the starting iron complex is preserved during the cycloaddition reaction between α,β-unsaturated acyliron complexes and allyltins. We are further studying the mechanism of this reaction and examining possible synthetic applications. In addition we are further investigating the scope and stereoselectivity of the novel destannylation reaction presented in Scheme 2.

Acknowledgements: We wish to thank the National Institutes of Health (GM-40777) for support of this research.

References:

1. a. Herndon, J.W. *J. Am. Chem. Soc.* **1988**, *109*, 3165 - 3166. This reaction is reminiscent of the reaction of allyltransition metal complexes with highly electron-deficient alkenes. b. Cutler, A.; Ehntholt, D.; Giering, W.P.; Lennon, P.; Raghu, S.; Rosan, A.; Rosenblum, M.; Tancrede, P.; Wells, D. *J. Am. Chem. Soc.* **1976**, *98*, 3495 - 3507. c. Lee, G.-H.; Peng, S.-H.; Yang, G.-M.; Lush, S.-F.; Liu, R.-S. *Organometallics* **1989**, *8*, 1106 - 1111.

2. Synthesis of pure *trans*- or *cis*-Crotyltributylstannane is difficult. a. Mutarasso-Tchiroukhine, E.; Cadiot, P. *J. Organometal. Chem.* **1976**, *121*, 155 - 168. b. Mutarasso-Tchiroukhine, E.; Cadiot, P. *J. Organometal. Chem.* **1976**, *121*, 169 - 176.

3. Quinn, S.; Shaver, A. *Inorg. Chim. Acta* **1980**, *38*, 243 - 245. b. The reaction of a mixture of E- and Z-crotonyl chloride with Fp anion has been reported to yield the E- and Z-crotonyliron. Ojima, I.; Kwon, H.B. *Chem. Lett.* **1986**, 1327 - 1330.

4. a. Davies, S.G.; Jones, R.H.; Prout, K.H.; *Tetrahedron* **1986**, *42*, 5123 - 5127. b. Liebeskind, L.S.; Welker, M.E.; Fengl, R.W. *J. Am. Chem. Soc.* **1986**, *108*, 6328 - 6342.

5. Spectral data for **4A**: ^{1}H NMR ($CDCl_3$): δ 4.82 (s, 5H); 3.07 (q, 1H, J = 7.5); 1.8 - 2.5 (m, 5H); 1.46 (m, 7H); 1.32 (m, 6H); 0.99 (d, 2H, J = 6.9); 0.85 (m, 15H). ^{13}C NMR (C_6D_6): 253.9, 215.5, 86.7, 83.1, 41.7, 39.3, 34.9, 29.9, 29.8, 27.8, 22.1, 13.8, 8.6. IR (neat): 2010 (s); 1950 (s); 1644 (s). Spectral data for **4B**: ^{1}H NMR ($CDCl_3$): δ 4.76 (s, 5H); 3.52 (q, 1H, J = 7.3); 1.9 - 2.4 (m, 2H); 1.1 - 1.7 (m, 17H); 0.65 - 0.90 (m, 17H). ^{13}C NMR (C_6D_6): 259.1, 214.8, 214.6, 86.5, 79.0, 38.9, 38.1, 32.8, 29.3, 27.4, 18.5, 16.2, 13.6, 8.30. IR (neat): 2012 (s); 1953 (s); 1648 (s). The stereochemistry of the tributyltin group could not be assigned reliably for either **4A** or **4B**.

6. Danheiser, R.L.; Carini, D.J.; Fink, D.M.; Basak, A. *Tetrahedron* **1983**, *39*, 935 - 947.

7. Spectral data for **7**: ^{1}H NMR ($CDCl_3$): δ 7.38 (br s, 5H); 5.15 (s, 2H); 4.42 (m, 1H); 2.71 (q, 1H, J = 9.2); 2.08 - 2.40 (m, 4H); 1.95 (m, 1H);1.65 (br s, 1H); 1.16 (d, 3H, J = 7.2). ^{13}C NMR ($CDCl_3$): δ 175.4, 136.2, 128.5, 128.1, 127.9, 72.6, 66.1, 49.8, 44.1, 39.9, 37.5, 20.3. IR(CH_2Cl_2): 3607 (m); 3460 (br, m); 1728 (s). For spectra of a similar compound, see: Gaultieri, F.; Angeli, P.; Giannella, M.; Melchiorre, C. *Syn. Commun.* **1976**, *6*, 63 - 68.

(Received in USA 17 July 1989)