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Supplementary Material Available: General method for synthesis of carbamates **3**, characterization of carbamates **3**, and general method for reactions of carbamates **3** (2 pages). Ordering information is given on any current masthead page.

Reaction of Allylstannanes with α,β-Unsaturated Acyliron Complexes: A Novel [3 + 2] Cycloaddition Reaction

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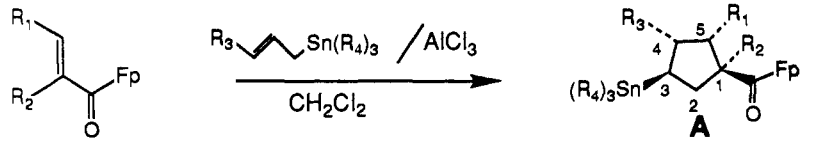
Recently, α,β-unsaturated acyliron complexes have emerged as valuable synthetic intermediates.[1] They undergo reactions such as Michael addition of nucleophiles[2] and Lewis acid catalyzed Diels–Alder reactions[3] readily. Also, they have seen recent application toward stereoselective synthesis.[1,3b,c] As part of a study to probe Lewis acid catalyzed reactions of acryloyliron complexes **1** with olefin and diene substrates,[3a] we recently initiated a study of the reactions of **1** with allylstannanes. As shown in Scheme I, this process catalyzed by aluminum chloride does not give the expected 5-hexenoyl species **4**[4] but provides the unexpected five-membered ring adduct **3**. We herein discuss preliminary results from studies of this remarkable reaction which potentially serves as a novel and useful method for cyclopentanoid synthesis.

Allyltributyltin reacts with acryloyliron complex **1** at −26 °C in the presence of 1 equiv of aluminum chloride to give the cyclopentanoid compound **3** in 42% yield. This appears to be a general reaction for five-membered ring formation as is evident from the examples provided in Table I. In two cases, the open-chain product analagous to compound **4** is observed (entries 8, 14). In all cases, only one stereoisomer is obtained as determined by ^{1}H NMR and ^{13}C NMR spectroscopy. Cis stereochemistry has been assigned to the reaction products based upon analysis of the ^{13}C–^{119}Sn coupling constants of selected compounds.[8] Optimum yields were obtained using freshly sublimed aluminum chloride as catalyst. Other catalysts were less effective for the five-membered ring-forming reaction. The acryloyl complex **1** is apparently unstable under the reaction conditions and decomposition competes with cycloaddition. This accounts for less than satisfactory mass balance seen in some cases.

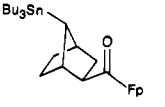
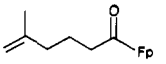
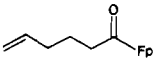
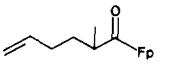
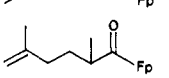
The mechanism we propose for this cycloaddition is outlined in Scheme I. First the aluminum chloride complexes with the acyliron giving the carbene complex **2**.[3a] The allylstannane then attacks the electrophilic carbene complex at C-2 giving the intermediate tin-stabilized carbocation **5**. This carbocation is stabilized by hyperconjugative interaction with the tributyltin group.[9] In the extreme, this interaction can be expressed by the nonclassical resonance form **5B**.[10] In **5B** there is significant electrophilic character at C-4 and C-5. Attack by the enolate at C-5 gives the five-membered ring compound **3**. Normally carbocations such as **5** destannylate to give olefins.[4,11] In this system, the favored pathway is cyclization. Here, iron donates significant electron density to the enolate in **5**, making it more reactive and making ring closure faster than with simple enolates.[12] The reaction efficiency also depends upon substituents at tin. The electron-donating alkyl groups provide better yields and faster reactions than the inductively electron-withdrawing phenyl groups.

This type of process has been observed in reaction of η^1-allyl transition-metal compounds with enones.[13] However, allenylsilanes are the only nontransition-metal systems which undergo

Table I. Reaction of α,β-Unsaturated Acylirons with Allystannanes



Fp = $Fe(CO)_2Cp$

entry	acyliron	allylstannane	catalyst	time/temp, °C	product	yield,[a,b] %
1	R_1, R_2 = H	allyltributyltin	$EtAlCl_2$	0.5 h/0	A: R_1, R_2, R_3 = H; R_4 = *n*-Bu	40
2	R_1, R_2 = H	allyltributyltin	$AlCl_3$	0.5 h/−26	A: R_1, R_2, R_3 = H; R_4 = *n*-Bu	42[6,15]
3	R_1, R_2 = H	allyltrimethyltin	$AlCl_3$	1.5 h/0	A: R_1, R_2, R_3 = H; R_4 = Me	27
4	R_1, R_2 = H	allyltriphenyltin	$AlCl_3$	24 h/25	A: R_1, R_2, R_3 = H; R_4 = Ph	8 (15)
5	R_1, R_2 = H	*trans*-crotyltributyltin	$AlCl_3$	1 h/0–25	A: R_1, R_2 = H; R_3 = Me; R_4 = *n*-Bu	52 (56)
6	R_1, R_2 = H	*trans*-cinnamyltributyltin	$AlCl_3$	2 h/25	A: R_1, R_2 = H; R_3 = Ph; R_4 = *n*-Bu	34 (45)
7	R_1, R_2 = H	cyclopent-2-enyltributyltin	$AlCl_3$	1 h/−78		27 (40)[7]
8	R_1, R_2 = H	methallyltributyltin	$AlCl_3$	5 min/−78		10
9	R_1 = H, R_2 = CH_3	allyltributyltin	$AlCl_3$	5 min/0	A: R_1, R_3 = H; R_2 = Me; R_4 = *n*-Bu	66 (91)
10	R_1 = H, R_2 = CH_3	*trans*-crotyltributyltin	$AlCl_3$	1 h/25	A: R_1 = H; R_2, R_3 = Me; R_4 = *n*-Bu	51 (87)
11	R_1 = CH_3, R_2 = H	allyltributyltin	$AlCl_3$	1 h/25	A: R_1 = Me, R_2, R_3 = H; R_4 = *n*-Bu	41 (58)
12	R_1, R_2 = H	allyltrimetylsilane	$AlCl_3$	24 h/25		31 (41)
13	R_1 = H, R_2 = CH_3	allyltrimethylsilane	$AlCl_3$	60 h/25		12 (77)
14	R_1 = H, R_2 = CH_3	methallyltributyltin	$AlCl_3$	5 min/−78		11 (57)

[a] The yields reflect compounds pure by TLC, ^{1}H NMR, and ^{13}C NMR analysis. The yields in parentheses are based on recovered starting material. [b] For a procedure see ref 5.

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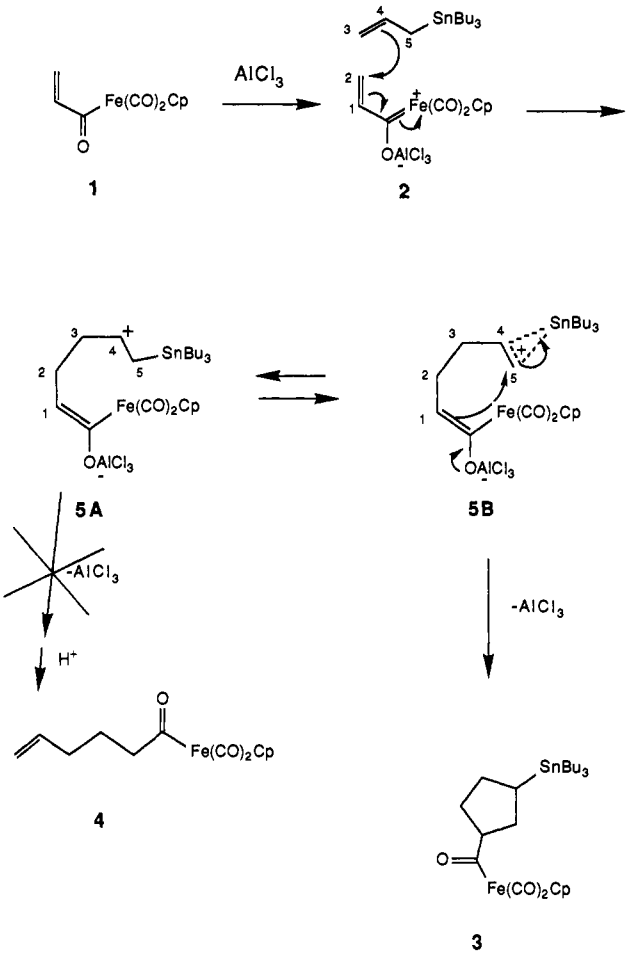
Scheme I



the analagous reaction with enones.[14] Interestingly, under identical conditions allyltrimethylsilane reacts with acryloyl complex **1** to give the 5-hexenoyl complex **4** exclusively. We believe this difference reflects lessened hyperconjugative stabilization of the β-carbocation **5** in the silicon case.[9] When methallyltributyltin reacts with **1** and $AlCl_3$, the only product isolated is the open-chain compound (entries 8, 14). Here, the intermediate carbocation **5B** is sterically destabilized and rapid destannylation occurs to give the open-chain compound. Alternatively, the intermediate carbocation more resembles **5A** (tertiary carbocation) and since in **5A** C-5 is not electrophilic, cyclization does not occur.

We are currently investigating this process with regard to mechanistic generalities and attempting to develop its synthetic potential for stereoselective five-membered ring construction.

Acknowledgment. We thank the State of Maryland and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for research support. In addition, we thank Professor Pat Mariano for helpful discussions.

Supplementary Material Available: Spectral characterization of products and discussion of stereochemical assignments (4 pages). Ordering information is given on any current masthead page.

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(5) All reactions were run under nitrogen and at 0.1 M concentration. A 1:1:1.1 ratio of acyliron/$AlCl_3$/allylstannane was used. To a mixture of acyliron and $AlCl_3$ at the indicated temperature was added the allylstannane. The reactions were run to completion or until no further reaction was noted (TLC). The reaction mixture was filtered through alumina and final purification was by flash chromatography on silica (slurry packed with 99:1 hexane/triethylamine).

(6) The stereochemistry of compound **4** (entries 1,2 of Table I) was assigned on the basis of ^{13}C-^{119}Sn coupling constants. The coupling constant between C_1 (74.2 ppm) and Sn was 42 Hz, which is more consistent with the cis orientation.[8]

(7) The coupling constant between the α-acyl carbon in this product and ^{119}Sn was 48 Hz. See: Kuivila, H. G.; Considine, J. L.; Sarma, R. H.; Mynott, R. J. *J. Organomet. Chem.* **1976**, *111*, 179-196.

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(10) A referee has suggested that **5B** forms directly. Undoubtedly there is interaction with the tin in the transition state,[9] and the timing of events will depend upon whether the initial intermediate resembles **5A** or **5B**.

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(15) **Note Added In Proof.** The reaction in entries 1 and 2 gives compound **3** in 64% yield (74% based on recovered starting material) with use of methylaluminum sesquichloride as catalyst.

Free Monomeric Metaphosphate in Protic Solution: Complete Racemization at Phosphorus in the *tert*-Butyl Alcoholysis of *p*-Nitrophenyl Phosphate

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The question of the intermediacy of monomeric metaphosphate in displacement reactions of phosphate monoesters has remained a controversial issue, despite efforts from many laboratories.[1] Several attempts have been made recently to obtain stereochemical information consistent with a dissociative pathway for the alcoholysis of [^{16}O,^{17}O,^{18}O]phosphate esters,[2-6] the most persuasive of which have demonstrated partial racemization at phosphorus in such displacement reactions in aprotic media. We now report the *complete* racemization at phosphorus in a simple phospho transfer reaction *in a protic solvent*, thus providing evidence for the intermediacy of a symmetrically solvated metaphosphate species in the solution reaction of a phosphate monoester.

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