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Hypervalent Organoiodine-Promoted Oxidative Ring Expansions of Tributylstannyl Lactols. New and General Synthesis of Unsaturated Medium-Ring Lactones#

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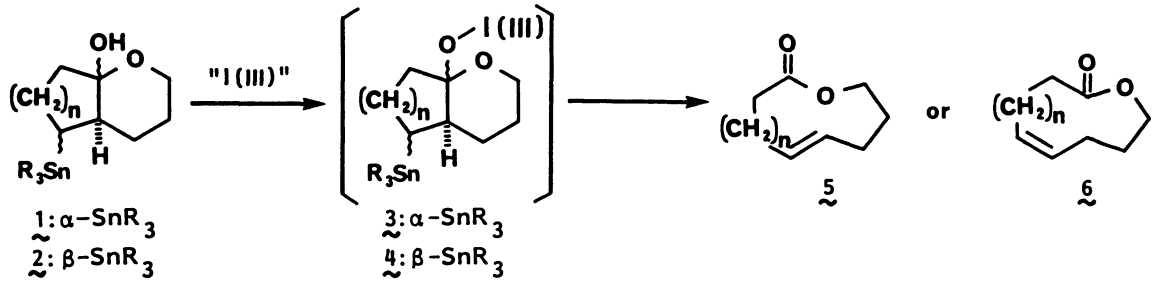
A new ring expansion route to olefinic lactones was developed. Oxidative 1,4-fragmentation of tributylstannyl lactols utilizing (diacetoxyiodo)bezene under mild conditions gave unsaturated medium-ring lactones stereospecifically in good yields. The relative stereochemistry of tributylstannyl group of the lactols determines the double bond geometry of the lactones.

There have been increasing interest in the development of new methodology for the synthesis of medium-sized lactones.[1,2] The most direct method is intramolecular cyclization, involving formation of the acyl-oxygen or carbon-carbon bond, of functionalized acyclic progenitors. Ring expansion of bicyclic systems constitutes an alternative,highly efficient route to medium-ring lactones.

Recently, we developed a new and efficient ring opening reaction of carbocycles that yields unsaturated carbonyl compounds by iodine(III)-mediated oxidative 1,4-fragmentation of γ-tributylstannyl alcohols.[3] The reaction was found to be stereospecific and applied to the synthesis of the mosquito pheromone, erythro-6-acetoxyhexadecan-5-olide.[4] The same type of fragmentation reaction utilizing lead tetraacetate in refluxing benzene was also reported by Isoe and his co-workers.[5,6] On the basis of these our findings, we have designed a new synthetic reaction that by the application of the hypervalent organoiodine-promoted oxidative 1,4-fragmentation reaction, trialkylstannyl lactols 1 and 2 would undergo a stereospecific ring expansion via the formation of 10-I-3 intermediates 3 and 4 to produce unsaturated medium-ring lactones 5 and 6, respectively (Scheme 1).



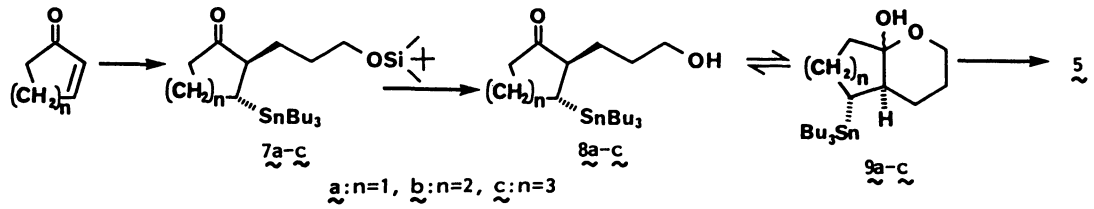
1: α-SnR3, 2: β-SnR3 — 3: α-SnR3, 4: β-SnR3 — 5 — 6

Scheme 1.

Dedicated to Professor Teruaki Mukaiyama on the occasion of his 60th birthday.

Synthesis of the required tributylstannyl alcohols 8 was carried out in a straightforward fashion as outlined in Scheme 2. Conjugate addition of tributylstannyllithium to cyclohex-2-en-1-one in tetrahydrofuran (THF) at -78 °C followed by alkylation of the resulting lithium enolate with 3-t-butyldimethylsiloxy-1-iodopropane (10) in the presence of hexamethylphosphoric triamide (HMPA) at -30 °C for 5 h afforded the trans-β-stannyl ketone 7b [7] stereoselectively in 76% yield. The corresponding cis-isomer 13 was not detected in the reaction mixture. Removal of the protecting group of 7b with tetrabutylammonium fluoride in THF gave an 81% yield of hydroxy stannane 8b, which predominantly exists as a stereoisomeric mixture of the lactol 9b.[8] The ratio of the trans- to cis-fused lactol 9b was determined to be 85:15 by the ^{13}C NMR spectrum : δ 97.1 [s, $^{3}J(^{119}Sn-^{13}C)$ = 58.6 Hz, C-1, trans-9b] and 96.2 (s, C-1, cis-9b). Similarly the conjugate addition-enolate alkylation reaction of cyclopent-2-en-1-one and cyclohept-2-en-1-one led to the stereoselective formation of the trans-ketones 7a (80%) and 7c (46%), respectively. Fluoride ion-induced deprotection gave rise to a good yield of hydroxyketones 8a and 8c. In contrast to the case of 8b, ^{13}C NMR analysis of 8a and 8c showed the absence of the corresponding lactol forms 9a and 9c.

Iodosylbenzene undergoes a facile oxidative 1,4-fragmentation of cyclic γ-stannyl alcohols.[3,4] Thus, exposure of the lactol 9b to iodosylbenzene in the presence of boron trifluoride etherate and dicyclohexylcarbodiimide produced the ten-membered-ring lactone 5 (n = 2)[7] through oxidative ring expansion but in a moderate yield (Table 1, entry 2). The use of (diacetoxyiodo)benzene (DAIB) as an alternative hypervalent organoiodine compound improved the yield dramatically: To a solution of 9b (490 mg, 1.10 mmol) in dichloromethane (10 ml) was added DAIB



Scheme 2.

Table 1. Oxidative ring expansion of hydroxyketones (8) or lactols (9)[a]

Entry	8 or 9	Reagent	Reaction conditions	Product 5	Yield[b] %
1	8a	(2) $C_6H_5I(OAc)_2$	rt(12 h)	n = 1	75
2	9b	(1.2) $(C_6H_5IO)n$/(1.4)DCC/ (1.2) BF_3-Et_2O	0 °C(1 h) then rt(1 h)	n = 2	49(52)
3	9b	(1.2) $C_6H_5I(OAc)_2$	rt(3 h)	n = 2	86(90)
4	8c	(1.2) $C_6H_5I(OAc)_2$/ (0.05) BF_3-Et_2O	0 °C(5 h)	n = 3	62[c]

a) The reactions were carried out in dichloromethane.

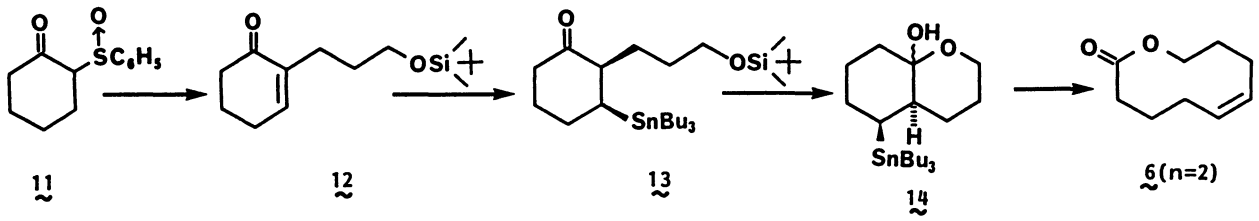
b) Yields refer to pure isolated materials. GLC yields are shown in parenthesis.

c) Stereoisomeric purity was shown to be higher than 95%.

(425 mg, 1.32 mmol) at room temperature under nitrogen, and the solution was stirred for 3 h. After evaporation of the solvent, purification by silica gel column chromatography [acetone-pentane (2:98)] gave 5 (n = 2, 145 mg, 86%). GLC (20% Silicone GE SF-96 on Chromosorb W at 140 °C) and ^{1}H NMR spectrum[7] showed the exclusive formation of the trans-lactone 5 (n = 2).

Ring expansion of the cyclopentanone 8a proceeded slowly compared to that of 9b and required an excess amount of DAIB (entry 1). Following two reasons may account for the fact : 1) The ring expansion of 8a should occur via the formation of the energetically unfavorable lactol form 9a . 2) Inspection of the molecular model of 9a shows a slight deviation from an ideal anti-coplanar arrangement between breaking C_1-C_6 and C_7-Sn bonds. Much more difficulties were encountered with the conversion of the hydroxy cycloheptanone 8c to trans-6-decen-10-olide (5) (n = 3)[7] and a large amount of 8c was recovered unchanged on the prolonged reaction with 3 equiv. of DAIB. The difficulties were overcome by the use of catalytic boron trifluoride etherate, which may activate DAIB by coordination to the oxygen atom and promote the rate of formation of the lactol 9c under the reaction conditions. Thus, a rapid and stereoselective ring expansion of 8c was observed (entry 4).

In order to illustrate the validity of our strategy concerning the control of stereochemical course of the expansions, the lactol 14 was synthesized. Alkylation of the sodium salt of the β-keto sulfoxide 11 with 10 in dimethylformamide at room temperature for 1 h,[9] accompanied by the spontaneous β-elimination of the phenylsulfinyl group, yielded directly the unsaturated ketone 12 in 42% yield. 1,4-Addition of tributylstannyllithium to 12 in THF [-78 °C (3 h) → -45 °C (0.5 h)] followed by kinetic protonation using methanol at -78 °C afforded the cis-β-stannyl ketone 13 [7] in 55% yield. ^{13}C NMR allows the assignment of stereochemistry in comparison of the coupling constant between carbonyl carbon and tin atoms of 13 with that of 7b: $^3J(^{119}Sn-^{13}C)$, 32.2 Hz for 13 and 44.9 Hz for 7b.[10] After pyridinium p-toluenesulfonate catalyzed deprotection of 13, the lactol 14 was treated with DAIB (2.6 equiv.) in dichloromethane at room temperature for 1.5 h. GLC of the reaction mixture showed the formation of cis-5-nonen-9-olide (6) (n = 2, 50%)[7] with high stereoisomeric purity (> 96%).



11 12 13 14 6(n=2)

Scheme 3.

On the basis of the results described above, it is possible to draw a conclusion that the stereochemistry of the iodine(III)-mediated oxidative ring expansion of stannyl lactols 1 and 2 is heavily dependent upon that of the stannyl group.

References

1) T. G. Back, Tetrahedron, 33, 3041 (1977); K. C. Nicolaou, ibid., 33, 683 (1977); S. Masamune, G. S. Bates, and J. W. Corcoran, Angew. Chem., Int. Ed. Engl., 16, 585 (1977).

2) S. L. Schreiber, J. Am. Chem. Soc., 102, 6163 (1980); S. L. Schreiber, B. Hulin, and W.-F. Liew, Tetrahedron, 42, 2945 (1986).

3) M. Ochiai, T. Ukita, Y. Nagao, and E. Fujita, J. Chem. Soc., Chem. Commun., 1984, 1007.

4) M. Ochiai, T. Ukita, Y. Nagao, and E. Fujita, J. Chem. Soc., Chem. Commun., 1985, 637.

5) K. Nakatani and S. Isoe, Tetrahedron Lett., 25, 5335 (1984); 26, 2209 (1985).

6) For an oxidative fragmentation of γ-hydroxysilanes by the reaction with ceric ammonium nitrate, see: W. S. Trahanovsky and A. L. Himstedt, J. Am. Chem. Soc., 96, 7974 (1974); S. R. Wilson, P. A. Zucker, C.-W. Kim, and C. A. Villa, Tetrahedron Lett., 26, 1969 (1985).

7) Selected ^{1}H NMR spectral data (400 MHz, $CDCl_3$) are as follows.
5(n=1): δ 1.70-1.82 (1H, m), 1.87-1.97 (1H, m), 2.08-2.48 (6H), 4.05(1H, ddd, J=12.0, 9.3, and 2.5 Hz), 4.54 (1H, m), and 5.46 (2H, m). Coupling constant between vinylic protons is 16.1 Hz.
5(n=2): δ 1.61 (1H, m), 1.75 (1H, m) 1.79-2.10 (5H), 2.23-2.33 (3H), 3.71 (1H, dt, J=11.7 and 3.4 Hz), 5.00 (1H, ddd, J=12.6, 11.7, and 1.8 Hz), 5.26 (1H, dddd, J=15.1, 10.3, 3.9, and 2.0 Hz), and 5.52 (1H, dddd, J=15.1, 10.8, 3.0, and 1.0 Hz)
5(n=3): δ 1.52 (2H, m), 1.72 (2H, m), 1.77 (2H, m), 1.90 (2H, dd, J=11.7 and 7.2 Hz), 2.15 (2H, dd, J=11.7 and 6.8 Hz), 2.20 (2H, m), 4.25 (2H, t, J=4.9 Hz), 5.27 (1H, dtt, J=15.1, 7.2, and 0.9 Hz), and 5.39 (1H, dtt, J=15.1, 6.8, and 0.8 Hz).
6(n=2): δ 1.74-1.85 (4H), 2.20-2.28 (4H), 2.30 (2H, dd, J=6.8 and 6.4 Hz), 4.19 (2H, t, J=6.4 Hz), and 5.31-5.41 (2H, m). Coupling constant between vinylic protons is 11.2 Hz.
7b: δ 0.04 (6H, s), 0.89 (9H, s), 0.79-0.97 (15 H), 1.31 (6H), 1.47 (6H), 1.62 (5H), 1.76 (2H, m), 1.97 (1H, m), 2.12 (1H, m), 2.38 (3H), and 3.59 (2H, m).
13: δ 0.04 (6H, s), 0.89 (9H, s), 0.73-0.95 (15H), 1.23-1.53 (16H), 1.80-2.03 (5H), 2.23 (1H, m), 2.48 (2H, m), and 3.59 (2H, t, J=6.3 Hz).

8) The presence of a small amount of the ring-opened ketonic form 8b was deduced from IR [1690 cm^{-1} (C=O)] and ^{13}C NMR [δ 214.6 (C=O)] spectra.

9) P. G. Gassman and G. D. Richmond, J. Org.Chem., 31, 2355 (1966).

10) Karplus-type dependence of vicinal ^{119}Sn-^{13}C coupling has been demonstrated to exist in a series of stereochemically rigid organotin compounds: D. Doddrell, I. Burfitt, W. Kitching, M. Bullpitt, C.-H. Lee, R. J. Mynott, J. L. Considine, H. G. Kuivila, and R. M. Sarma, J. Am. Chem. Soc., 96, 1640 (1974); G. Wickham, H. A. Olszowy, and W. Kitching, J. Org. Chem., 47, 3788 (1982).

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