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THE STEREOSPECIFIC FORMATION OF AN EXOCYCLIC ALKENE BY A CONSECUTIVE RADICAL CYCLIZATION-ELIMINATION

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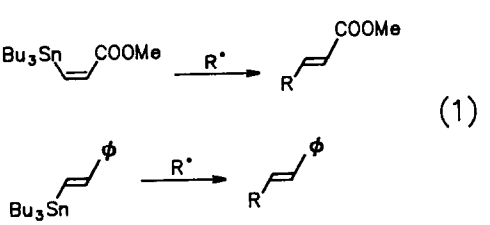
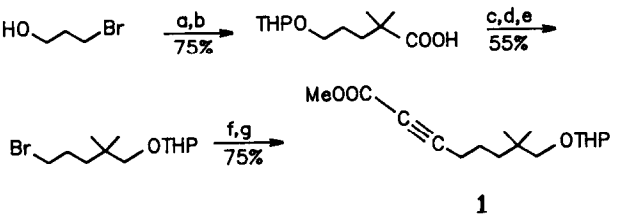
Abstract: The iodovinylstannanes 4 and 5 were prepared by the conjugate addition of the tri-n-butyltin moiety to a substituted propiolic ester. Compounds 4 and 5 underwent a radical cyclization-elimination reaction to stereospecifically generate an exocyclic alkene.

Recently Baldwin and co-workers reported a new method to form carbon-carbon bonds based on the addition of an alkyl radical to a β-stannyl acrylate followed by elimination of the trialkylstannyl radical.[1a] Subsequent studies showed that the reaction was stereoselective, giving the E geometry for the product regardless of the stereochemistry of the starting stannylalkene (eq. 1).[1b] Russell and co-workers have also shown that a variety of radicals will react with β-substituted styrenes, including vinyl stannanes, to give the coupled product of an addition-elimination reaction.[1c] In these examples, the starting (E)-styrene yields the E product. Following the pioneering work of Beckwith and co-workers on radical cyclizations,[2] there have been a number of reports of elegant uses of radical cyclizations in the synthesis of complex organic molecules.[3] The synthetic utility of these reactions arises from the facile synthesis of the starting materials, the mild conditions required to effect reaction, and the selectivity in the reaction pathways.



(1)

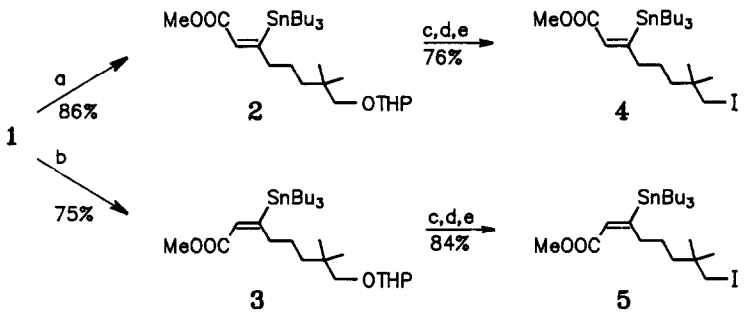
We would like to report the extension of the Baldwin radical addition-elimination sequence to intramolecular examples. The acetylenic ester 1 was prepared as shown below.



1

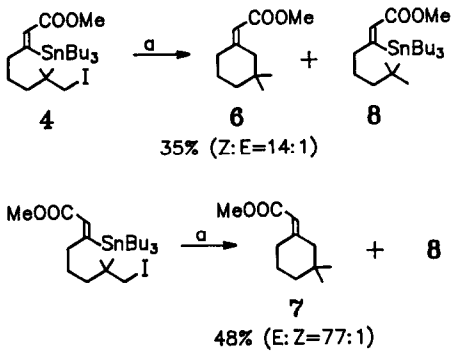
(a) dihydropyran, TsOH, CH_2Cl_2; (b) 2 x n-BuLi, $Me_2CHCOO^-(c\text{-}C_6H_{11})NH_2^+$, THF; (c) LAH, THF; (d) $Ph_3P\text{-}Br_2$, CH_2Cl_2; (e) dihydropyran, TsOH, MeOH; (f) LiCCH.EDA, DMSO; (g) MeLi, THF then ClCOOMe, THF.

This ester was used as the starting material for the isomeric vinylstannanes 2 and 3, which were prepared with high stereoselectivity using the procedure of Piers and co-workers.[4] Thus addition of (phenylthio)(tri-n-butylstannyl)cuprate at -40° to 1 gave the Z-vinyl stannane 2 in 86% purified yield. While addition of tri-n-butylstannyl copper - dimethyl sulphide at -78° gave the E-vinyl stannane 3 in 75% purified yield. The THP groups in 2 and 3 were cleaved in high yield. Initial efforts to prepare the xanthates of these alcohols led to decomposition of the starting material and/or product. The preparation of the thionocarbonate was also unsatisfactory. However, we were able to prepare the iodides 4 and 5 in excellent yield via an S_n2 displacement on the intermediate neopentyl triflates.[5]



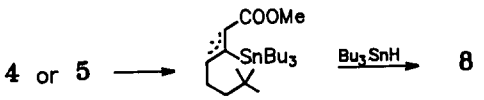
(a) [n-$Bu_3SnCuSPh$]Li, THF, -40°; (b) n-$Bu_3SnCu.Me_2S$, THF, -78°; (c) MeOH, TsOH; (d) $(CF_3SO_2)O$, py, CH_2Cl_2; (e) $(n\text{-}Bu)_4NI$, PhH, Δ;

The Z-iodide 4 was treated with tri-n-butylstannane and a catalytic amount of AIBN in warm benzene to give the cyclized product 6 and the reduced vinylstannane 8 in modest yield. Treatment of the E-iodide 5 under similar conditions gave the cyclized product 7 and the same reduced vinylstannane 8.

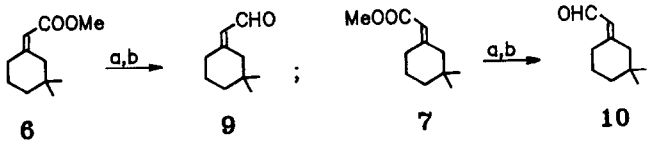


(a) $(\underline{n}\text{-Bu})_3SnH$, AIBN, PhH, 85°.

We have noted several features in these cyclizations. First and foremost was that the cyclizations are highly stereospecific and result from an addition-elimination sequence which involves "retention" of stereochemistry of the double bond.[6] The products are isomerized under the reaction conditions and hence the reactions were stopped before complete loss of starting iodide. The ratio of cyclized to reduced product was ca. 1:1 under a variety of conditions. The geometry of the reduced vinylstannane **8** was Z regardless of the geometry of the starting alkene. We suggest that the reduced product arises from an intramolecular hydrogen transfer[3g] to give an allyl radical which is then reduced by the tri-n-butylstannane to **8**. The geometry of **8** was assigned from the J_{Sn-H} for the vinyl proton and tin. This coupling constant was 108 Hz which is consistent with a trans relationship between the vinyl proton and the tin group.[7] The work of Piers and co-workers[4] suggests that the Z-isomer **8** is more stable than the corresponding E-isomer.



The relative rates of cyclization of **4** and **5** were quite different. The E-isomer **5** appears to undergo the cyclization reaction faster, in higher yield, and with higher stereoselectivity than **4**. These last two observations could be due to reaction and/or isomerization of the initially formed cyclized product under prolonged exposure to the reaction conditions. A separate experiment showed that both **6** and **7** were isomerized by AIBN in hot benzene. The stereochemistry of **6** and **7** was determined by comparing their spectral properties to those reported for authentic samples of these compounds.[8] In addition, **6** and **7** were converted into the boll weevil sex pheromones **9** and **10** following earlier syntheses.[8,9]



(a) LAH, Et_2O, Δ; (b) $CrO_3.py$, CH_2Cl_2.

Thus the intramolecular cyclization-elimination reaction of radicals offers a useful method to stereospecifically generate an exocyclic double bond. The scope of this reaction is under investigation, as are investigations to improve the yield of the cyclic products.[10]

References and Notes

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