INTERMOLECULAR ADDITION OF α-ALKOXYCARBONYL-β-STANNYLVINYL RADICALS TO ELECTRON-DEFICIENT ALKENES. SIMPLE ADDITION AND [2+2+2] ANNULATION REACTIONS

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Abstract: Regio- and stereocontrolled synthesis of vinylstannanes was achieved by intermolecular addition reaction of α -alkoxycarbonyl- β -stannylvinyl radicals to activated alkenes. Under high dilution conditions cyclohexene derivatives were obtained via [2+2+2] radical annulation reaction.

Recently we reported facile synthesis of α -methylenelactones and α -methylenecycloalkanones via intramolecular cyclization of α -alkoxycarbonyl- β -stannylvinyl radicals.¹ To further define the scope of the reaction of these vinyl radicals, their intermolecular addition reaction with substituted alkenes was studied.

Reaction of ethyl propiolate (1) with various alkenes 2 (3eq.) in the presence of tributylstannane (1eq.) and AIBN (0.1eq.) in benzene (0.2M) under reflux resulted in the formation of hydrostannation products 3 (E and Z isomeric mixture) and intermolecular addition products 4 in moderate yields (Scheme 1). In agreement with observations made in the study of intramolecular cyclization reaction of α -alkoxycarbonyl- β -stannylvinyl radicals, reaction with electron-deficient alkenes were inactive towards α -alkoxycarbonyl- β -stannylvinyl radicals. It is also worth noting that only Z isomers of vinyl stannanes 4 were obtained.

(Scheme 1)

| CO ₂ Et + (1) | $ \begin{array}{c} Bu_3SnH \\ \hline E \\ \underline{AIBN} \\ Benzene(0.2M) \\ 2h, 1 \\ 3eq) \end{array} $ | ^{Bu₃Sn₂ ^{CO₂Et} +} | $- \underbrace{(4)}_{E}^{\mathrm{Bu}_{3}\mathrm{Sn}} \underbrace{(2)}_{E}^{\mathrm{CO}_{2}\mathrm{Et}}$ |
|-----------------------------|--|---|---|
| a) | ∧ _{CO₂Me} | 62 %(Z:E=3:1) | 31 % |
| ъ) | ∕ _{CN} | 40 %(Z:E=3:1) | 52 % |
| c) | CO ₂ Me | 51 %(Z:E=3.2:1) | 38 % |
| d) (| <u>`</u> | 75 %(Z:E=2.7:1) | 11 % |
| e) 💋 | ∧ _{OAc} | 91 %(Z:E=2.9:1) | |
| f) | ∧ _{OBu} | 85 %(Z:E=3:1) | |

Vinylstannanes are of increasing importance as intermediates in synthetic organic chemistry.² Owing to their great versatility as building blocks for synthesis, considerable effort has been devoted to the regio- and stereocontrolled synthesis of vinylstannanes.³ The above method should provide an alternative way for their production, which should lead to stereoselective synthesis of trisubstituted olefins.

Slow addition of tributylstannane (0.5eq.) to a more diluted solution (0.1M) of ethyl propiolate (1) and electron-deficient alkenes 2 (5eq.) provided cyclohexene derivatives in moderate yields (Scheme 2).

The new products are believed to be obtained by the [2+2+2] triple radical Michael addition reactions. Recently, cyclopentane ring annulation by a [3+2] radical cycloaddition reaction has been reported.⁴ The unprecedented [2+2+2] triple radical Michael annulation represents a novel radical cycloaddition scheme for preparation of substituted cyclohexene rings (Scheme 2).

(Scheme 2)



NMR spectra and GC analysis show that annulation product 5a and 5b consists of 1:1 mixture of the double bond isomers. The product 5c was obtained as a single isomer.

Mechanistically, these annulation products are considered to be formed via the following reaction sequence (Scheme 3); 1) generation of a *a*-alkoxycarbonyl- β -stannylvinyl radical via intermolecular addition of a stannyl radical to the propiolate, 2) intermolecular addition of the vinyl radical to an activated alkene, 3) subsequent intermolecular addition of the alkyl radical to another molecule of the same alkene, 4) intramolecular 6-endo cyclization, 5) β -elimination of the stannyl radical (Scheme 3).

(Scheme 3)



In conclusion, it is apparent that intermolecular addition reaction of α -alkoxycarbonyl- β stannylvinyl radicals with activated alkenes affords a useful method for carbon-carbon bond formation.

Acknowledgements: The present study was supported by the Organic Chemistry Research Center (KOSEF).

References and Notes

- 1. 2.
- 3.
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(Received in Japan 29 June 1991)