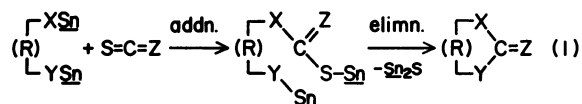


Cyclization Reaction of Bis(tributylstannylated) α -Ketols with Heterocumulenes. Preparation of *O,O*-Vinylene Imino- and Thiocarbonates

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(Received September 27, 1982)

Synopsis. Aromatic α -ketols reacted with diethylaminotributylstannane at 60 °C to afford a mixture of (*Z*)- and (*E*)-1,2-bis(tributylstannyloxy)-1,2-diarylethenes, which were allowed to react with organic isothiocyanates and carbon disulfide to give substituted *O,O*-vinylene imino- and thiocarbonates, respectively. Aliphatic α -ketol, 3-hydroxy-2-butanone, was treated by the aminostannane, followed by the reaction with carbon disulfide to form (*E*)-1,2-bis(tributylstannylthio)-2-butene.

β -Keto derivatives of the group IV organometalloids are well documented.^{1,2} These metalloid compounds are generally used as their tautomers, organometallic enol ethers, which are important intermediates in many kinds of carbon-carbon bond formation.² Our interest has been focused on both the reactivities of heteroatom-Sn bonds and the cyclization reaction of the saturated compounds having two heteroatom-Sn bonds with sulfur-containing heterocumulenes to form heteroatom-carbon bonds in carbonate syntheses (Eq. 1).

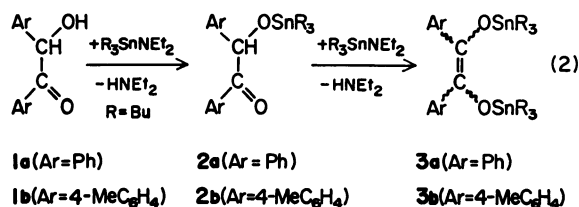


X, Y, Z = O, S, or NR'; (R) = (CH₂)_{2,3}; Sn = Bu₃Sn or Bu₂Sn/2

This work describes a bis(tributylstannylation) reaction of α -ketol to form bis(tributylstannyloxy)ethenes and their reactions with heterocumulene such as organic isothiocyanates or carbon disulfide to afford imino- or thiocarbonic *O,O*-diester.

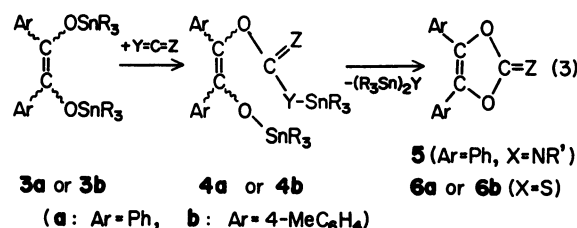
Results and Discussion

Formation of Bis(tributylstannyloxy)ethenes. Aromatic α -ketol, 2-hydroxy-1,2-diphenylethane-1-one (**1a**), was allowed to react with an equimolar amount of diethylaminotributylstannane at room temperature to form *O*-tributylstannylated compound (**2a**). A second mole of the aminostannane was added to **2a**, and the mixture was heated at 60 °C to accomplish the stannylation of α -H of carbonyl group in **2a**; this was followed by tautomerization (or *vice versa*) to give **3a** (Eq. 2). The reddish brown liquid (**3a**), prepared *in situ*, showed the strong band of (*E*)-C=C group at 1680 cm⁻¹, the weak band of (*Z*)-C=C group at 1640 cm⁻¹, and the strong band of vinyloxy group at 1330 cm⁻¹ in its IR spectrum. These data will suggest that the bis(tributyl-



stannylated) compound (**3a**) exists as a mixture of (*E*)- and (*Z*)-bis(tributylstannyloxy)ethenes. A mixture of (*E*)- and (*Z*)-bis(tributylstannyloxy)-1,2-bis(4-methylphenyl)ethenes (**3b**) was also obtained from the reaction of 2-hydroxy-1,2-bis(4-methylphenyl)ethane-1-one (**1b**) and two equivalents of diethylaminotributylstannane.

Cyclization Reaction of 3 with Heterocumulenes. An equimolar reaction of **3a**, prepared *in situ* from **1a** and the aminostannane, with phenyl isothiocyanate at room temperature gave a small amount of 2-phenylimino-4,5-diphenyl-1,3-dioxolene (**5**; R' = Ph).



Furthermore, **5** (R' = Ph) was formed in an improved yield (80%), when the reaction mixture was heated for 2 more hours at 100 °C. These results suggest that (*E*)-**3a** will slowly isomerize to (*Z*)-**3a**, which is easily cyclized with an isothiocyanate to give a high yield of **5a**.

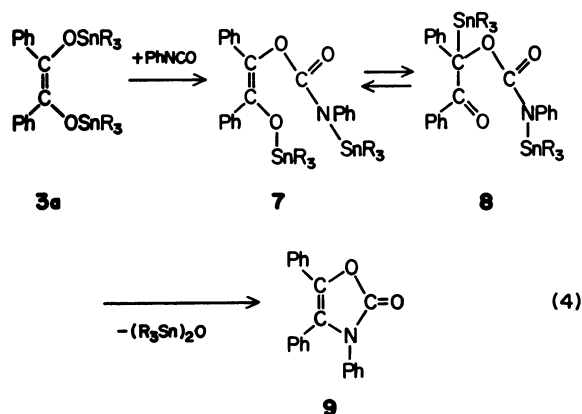
4-Methylphenyl isothiocyanate was also allowed to react with **3a** to afford **5** (R' = 4-MeC₆H₄). Aliphatic isothiocyanates such as ethyl and cyclohexyl isothiocyanates were less reactive and reacted partially even under severe reaction conditions.

Carbon disulfide is known to be a thiocarbonylating reagent for bis(organostannyloxy)alkanes.³ Here, unsaturated bis(organostannyloxy) compound, **3a** or **3b**, was submitted to a reaction with an excess amount of carbon disulfide under reflux for 24 h to afford the substituted *O,O*-vinylene thiocarbonate (**6a** or **6b**) in a moderate yield.⁴ On the occasion, *O,O*-vinylene thiocarbonate was prepared from **1** and thiophosgene⁵ or from vinylen carbonate and phosphorus pentasulfide.⁶ Therefore, the reaction (Eqs. 2 and 3) gives a new route to prepare **6** from the aminostannane, carbon disulfide, and **1**.

Carbonyl sulfide and carbon dioxide inserted across the Sn-O bond in **3a** to afford **4a** (X=O, Y=S or O). However, the starting material **3a** was recovered by distillation. Thus carbonylation of the enediol-type organostannyl compound **3a** was unsuccessful.

Phenyl isocyanate was reported to react with saturated bis(organostannyloxy) compound to form a carbamate-type adduct which was never cyclized even under severe reaction conditions.³ Bis(organostannyl) enediol-type compound (**3a**) reacted with the isocyanate for 7 h under reflux in toluene to afford 3,4,5-triphenyl-2(3*H*)-oxazolone (**9**). In the light of the scheme for the reaction

of vinylene carbonate with amines to form 2(3*H*)-oxazolones, reaction path (4) was tentatively proposed.



Organostannylation of Aliphatic α -Ketol and Its Reaction with Carbon Disulfide.

When 3-hydroxy-2-butanone (**10**) was allowed to react with diethylaminotributylstannane at 60 °C, the methine proton signal in **10** completely disappeared, and methyl and butyl signals only were observed in the NMR spectrum of the reaction mixture; this suggests the formation of bis(tributylstannylated) compound (**11**), which will exist mainly as an (*E*)-enediol-type organostannyl compound, because the band of (*E*)-C=C bond appeared in its IR spectrum. The compound (**11**) reacted with carbon disulfide to form not the corresponding *O,O*-vinylene thiocarbonate but (*E*)-2,3-bis(tributylstannylthio)-2-butene (**12**). Transformation of the bis(organostannyloxy)ethene (**11**) to the bis(organostannylthio)ethene (**12**) is a new type of the reaction of organostannyl-oxygen bond with sulfur-containing heterocumulene.⁸⁾

Experimental

Reaction of 1a with Diethylaminotributylstannane. The compound **1a** (2.12 g, 10.0 mmol) and diethylaminotributylstannane (3.36 g, 10.0 mmol) were stirred under dry nitrogen atmosphere and then *in vacuo* at room temperature to form a transparent liquid (**2a**). IR (neat) 1720 cm⁻¹ (C=O); NMR (CCl₄) δ =6.04 (s, 1H, CH). Subsequently, diethylaminotributylstannane (3.36 g, 10.0 mmol) was added to **2a**, and heated at 60 °C for 2 h *in vacuo* to form a reddish brown liquid (**3a**). **3a** could be isolated neither by vacuum distillation nor by recrystallization. **3a**: IR (CCl₄) 1640 ((*Z*)-C=C), 1690 ((*E*)-C=C), and 1330 cm⁻¹ (C=C-O).

Reaction of 3a with Aryl Isothiocyanate. Aryl isothiocyanate (10 mmol) was added to **3a** (10 mmol), prepared *in situ*, at room temperature. Soon after the addition, a small amount of white crystals of **5** were precipitated. Then, the reaction mixture was heated at 100 °C for 1 h, filtered, and washed with hexane to afford crude **5**. **5** (R'=Ph): yield 80%; MS *m/e* 313 (M⁺); IR (CHCl₃) 1730 (C=N) and 1680 cm⁻¹ (C=C); NMR (CDCl₃) δ =7.3–7.6 (15H, Ph), and **5** (R'=4-MeC₆H₄): yield 60%; mp 148–149 °C; MS *m/e* 327 (M⁺); IR (CHCl₃) 1735 (C=N) and 1680 cm⁻¹ (C=C); NMR (CDCl₃) δ =7.1–7.4 (14H, br., Arom.) and 2.30 (3H, s, CH₃). Found: C, 80.50; H, 5.25; N, 4.31%. Calcd for C₂₂H₁₇NO₂: C, 80.71; H, 5.23; N, 4.23%.

Reaction of 3a or 3b with Carbon Disulfide. The compound (**3a** or **3b**; 5.3 mmol) was allowed to react with carbon disulfide (1.5 ml) for 24 h under reflux. Hexane was added to the

reaction mixture to precipitate crystals of **6a** or **6b**. **6a**: yield 50%; mp 118–119 °C (Ref. 6 124 °C); IR (CCl₄) 1310 cm⁻¹, and **6b**: mp 183–184 °C; IR (CHCl₃) 1320 cm⁻¹; NMR (CDCl₃) δ =2.32 (6H, s, CH₃) and 7.3 (8H, d,d-type, Arom.). Found: C, 72.31; H, 5.03; S, 11.12%. Calcd for C₁₇H₁₄O₂S: C, 72.31; H, 5.00; S, 11.36%.

Reaction of 3a with Phenyl Isocyanate. Phenyl isocyanate (0.92 g, 7.1 mmol) was added to **3a** (4.9 mmol) in methylbenzene (8 ml) to form **7**; IR 1570 and 1590 cm⁻¹. The reaction mixture was refluxed for 6 h and distilled to remove the solvent. Hexane was added to the residue to separate white crystals of **9**; yield 70%; mp 191–193 °C; IR (CHCl₃) 1760 (C=O) and 1685 cm⁻¹ (C=C); NMR (CH₂Cl₂) δ =7.0–7.6 (15H, m, Ph). Found: C, 80.52; H, 5.04; N, 4.32%. Calcd for C₁₉H₁₅NO₂: C, 80.52; H, 4.82; N, 4.47%.

Treatment of 10 with Diethylaminotributylstannane Followed by the Reaction with Carbon Disulfide.

Acetoin (**10**; 2.25 g, 25.2 mmol) was treated with two equivalents of diethylaminotributylstannane (21.6 g, 58.6 mmol) *in vacuo* at 60 °C for 5 h to form the bis(tributylstannylated) compound (**11**); IR 1685 cm⁻¹ (C=C); NMR (CDCl₃) δ =1.8 (6H, br., CH₃) and 0.8–1.9 (m, BuSn). **10** was refluxed with an excess of carbon disulfide. The reaction mixture was then submitted to the sublimation under vacuum (10 Pa) at 130 °C to separate a small amount of **11**; mp 84.5–86.0 °C; MS *m/e* 698 (M⁺); IR (CHCl₃) 960 cm⁻¹ ((*E*)-C=C); NMR (CCl₄) δ =0.7–1.6 (54H, m, Bu) and 1.92 (6H, s, CH₃). Found: C, 48.14; H, 8.85; S, 9.04%. Calcd for C₂₈H₈₀S₂Sn₂: C, 48.16; H, 8.66; S, 9.04%.

The present work was partially supported by Grant-in-Aid for Scientific Research No. 165197 from the Ministry of Education, Science and Culture.

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- 8) The Mechanism of the formation of **12** has not been established. A probable scheme is the addition of CS₂ on O-Sn bond in 3-tributylstannyl-3-tributylstannyloxy-2-butanone, an isomer of **11**, to give the xanthate, which will isomerize to dithiocarbonic *S,S*-diester, followed by the elimination of COS to afford 3-tributylstannyl-3-tributylstannylthio-2-butanone, an isomer of 3-tributylstannyl-3-tributylstannyloxybutane-2-thione. These reaction will be repeated again to give **12**.