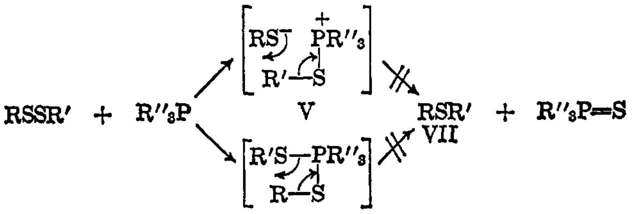
IV

concerted breakdown of a pentacovalent species, VI, are thus ruled out as primary product-determining reaction modes.



VI

$R = CH_2C_6H_4Br$
$R' = CH_2C_6H_4C_6H_5$
$R'' = NEt_2$

If either transformation depicted by V or VI were exclusively operating, only sulfide VII would have been observed.[11] Preliminary observations on the kinetics of this reaction have indicated that the mechanism is, however, more complicated than originally anticipated. Work is continuing in this area.

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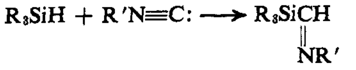
Radical Reaction of Isocyanide with Organotin Hydride

Sir:

Recently we reported a novel insertion reaction of isocyanide into a silicon–hydrogen linkage by a copper catalyst, a new type of hydrosilation.[1]



$$R_3SiH + R'N{\equiv}C\colon \longrightarrow R_3Si\underset{\underset{\displaystyle NR'}{\|}}{CH} \qquad (1)$$

Attempted copper-catalyzed insertion of isocyanide into the tin–hydrogen linkage of organotin hydrides proved unsuccessful. Instead, we found a new radical reaction of isocyanide with trialkyltin hydride in which trialkyltin (iso)cyanide[2] (I) and the hydrocarbon II were produced in fairly high yields.

$$R_3SnH + R'N{\equiv}C\colon \longrightarrow \underset{\text{I}}{R_3SnCN} + \underset{\text{II}}{R'H} \qquad (2)$$

Under a nitrogen atmosphere, a mixture of benzyl isocyanide (14.0 mmol), tri-*n*-butyltin hydride (14.0 mmol), and di-*t*-butyl peroxide (6 mol % for isocyanide) was stirred at 120–130° for 8 hr. The reaction mixture, which solidified on cooling at room temperature, was washed with cold ether. The insoluble crystalline solid on recrystallization from ether gave 3.63 g (11.5 mmol, 82%) of tri-*n*-butyltin (iso)cyanide (III), mp 88–89° (lit.[3] 88.5°). *Anal.* Calcd for $C_{13}H_{27}NSn$: C, 49.40; H, 8.61; N, 4.43. Found: C, 49.11; H, 8.80; N, 4.26. The ir spectrum and the glpc retention time of III were identical with those of an authentic sample prepared from tri-*n*-butyltin chloride and potassium cyanide.[4] The ether washings of the cooled reaction mixture were analyzed by glpc and contained 1.25 g (13.6 mmol, 97%) of toluene.

Similarly, the reaction of cyclohexyl isocyanide with tri-*n*-butyltin hydride induced by azobis(isobutyronitrile) in benzene produced III (52%) and cyclohexane (47%).

Reaction 2 requires a free-radical initiator. Heat treatment of a mixture of isocyanide and tri-*n*-butyltin hydride without a radical initiator under nitrogen gradually produced hexa-*n*-butyldistannane. Perhaps isocyanide played the role of a base catalyst for the coupling reaction of trialkyltin hydride.[5] In the radical-initiated reaction of isocyanide with trialkyltin hydride, distannane was formed only in small quantities.

Considering the necessity of a radical initiator and the generally known, high reactivity of organotin hydride toward free radicals,[5] the following scheme may outline the course of reaction.

$$R_3SnH \xrightarrow{\text{free radical}} R_3Sn\cdot$$

$$R_3Sn\cdot + R'N{=}C\colon \longrightarrow R'N{=}\dot{C}SnR_3 \xrightarrow{\beta\text{ scission}} R'\cdot + R_3SnCN$$

$$R'\cdot + R_3SnH \longrightarrow R'H + R_3Sn\cdot$$

As to the nature of the radical R'· in the above scheme, the reaction of *t*-butyl isocyanide with tri-*n*-butyltin hydride with the aid of azobis(isobutyronitrile) was examined. In the reaction at the reflux temperature of benzene as solvent for 24 hr the products were isobutane (45% yield) and III (51% yield). Isobutylene was not detected here. This observation has an interesting bearing on the character of the radical reaction of isocyanide.

Detailed mechanistic investigation will be the subject of future studies.

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Mass Spectrometry of Nucleic Acid Components. Trimethylsilyl Derivatives of Nucleotides, Nucleosides, and Bases[1]

Sir:

Although the potential value of mass spectrometry in the structure elucidation of nucleosides and related

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