was heated with cyclooctene (5.02 g (45.55 mmol)) in the presence of a small amount of CuCl at 55 °C for 2.5 h. The crude product was purified by chromatography with heptane: yield 3.4 g (88%) of pale yellow crystalline solid; mp 141 °C (hexane); ^{31}P NMR (CH_2Cl_2) δ −168.7 ($^1J(^{31}P-^{183}W)$ = 253.9 Hz) (isomer a), δ −173.0 ($^1J(^{31}P-^{183}W)$ = 253.9 Hz) (isomer b); IR (decalin) ν(CO) 2064 (w), 1942 (s), 1908 (vw) cm^{-1}; ^{1}H NMR (C_6D_6) δ 1.16 (br m, $(CH_2)_6$), 1.4–1.75 (m, 2 H, CH), 1.90 (dd, $^3J(H-H)$ = 6.35 Hz, $^2J(P-H) \approx$ 8 Hz, 2 H, PCH_2), 4.9–5.8 (m, 3 H, $CH{=}CH_2$); mass spectrum (EI, 70 eV, ^{184}W), *m/e* (relative intensity) 506 (M, 25), 478 (M − CO, 5), 396 ($(OC)_5WP-C_3H_5$, 15), 368 ($(OC)_4WP-C_3H_5$, 16), 340 ($(OC)_3WP-C_3H_5$, 35), 327 ($(OC)_4WP$, 38), 312 ($(OC)_2WP-C_3H_5$, 100), 299 ($(OC)_3WP$, 25), 284 ($OCWP-C_3H_5$, 22), 271 ($(OC)_2WP$, 19). Anal. Calcd for $C_{16}H_{19}O_5PW$: C, 37.97; H, 3.78; P, 6.12; W, 36.32. Found: C, 38.11; H, 3.85; P, 6.04; W, 35.26.

Registry No. **1**, 101376-96-9; **2**, 101376-97-0; **3**, 101376-98-1; **4**, 101376-99-2; **5**, 101377-00-8; **6**, 101377-01-9; **7**, 101377-02-0; **8**, 101377-03-1; **9**, 101377-04-2; **11**, 101377-05-3; **12**, 101377-06-4; **13**, 101377-07-5; **14**, 101377-08-6; **15**, 101377-09-7; **16**, 101377-10-0; **17**, 101377-11-1; **18**, 101377-12-2; **20**, 101377-13-3; **21a**, 101377-14-4; **21b**, 101469-67-4; $W(CO)_6$, 14040-11-0; $PhC{\equiv}CPh$, 501-65-5; $MeC{\equiv}CPh$, 673-32-5; 1-phenyl-3,4-dimethylphosphole, 30540-36-4; allyl chloride, 107-05-1; 1-butyl chloride, 109-69-3; *tert*-butyl chloride, 507-20-0; allyl bromide, 106-95-6; 4-bromobutene-1, 5162-44-7; 5-bromopentene-1, 1119-51-3; dimethyl acetylenedicarboxylate, 762-42-5; hexyne-3, 928-49-4; *trans*-stilbene, 103-30-0; cyclooctene, 931-88-4.

Reactivity Profile of 1,3-Disubstituted Tetraorganodistannoxanes Assessed in Urethane Formation Reaction[1]

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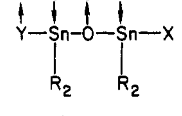
Received October 23, 1985

For the purpose of assessing general reactivity profiles of 1,3-disubstituted tetraorganodistannoxanes, the catalytic mechanism of the urethane formation reaction was investigated in detail. Apparently, the reaction is initiated by the formation of tin alkoxides which then add to isocyanates to give stannylcarbamates. Alcoholysis of these compounds furnishes urethane and regenerates tin alkoxides. In these reactions, an Sn–X (X = halogen, NCS) or Sn–OH bond in distannoxanes is easily cleaved by alcohols. The unique reactivity can be ascribed to the heteroatom-bridged dimerization of distannoxanes. For the reaction of alkoxydistannoxanes with isocyanates, a template effect is suggested by which addition reaction occurring at the tin attached to an alkoxyl group is accelerated by the tin of the other chain in the dimeric formulation.

Introduction

Among various organometallics of the group 14 elements, diorganotin dihalides are unique in that they can provide stable partial hydrolysis products, 1,3-disubstituted tetraorganodistannoxanes (1).[2] The facile formation and stability of these compounds are attributable to the dimeric ladder structure which has been confirmed both in the solid state and in solution.[3] Moreover, it is now apparent that replacement of one of the halogens in 1,3-dihalodistannoxanes with a hydroxy or alkoxy group leads to 3-halo-1-hydroxy- or 3-halo-1-alkoxydistannoxanes having the oxygen-bridged structure (Y = OH or OR in 1).



1a–**j**, R = Bu

a, X = Cl, Y = Cl; **b**, X = Cl, Y = OH; **c**, X = Cl, Y = OPh; **d**, X = Br, Y = Br; **e**, X = Br, Y = OH; **f**, X = Br, Y = OPh; **g**, X = NCS, Y = NCS; **h**, X = NCS, Y = OH; **i**, X = NCS, Y = OPh; **j**, X = NCS, Y = OMe

In contrast to the extensive structural studies, few have been reported on their reactions or synthetic applications. One such example is the distannoxane-catalyzed urethane formation discovered by Yokoo et al. in 1967, who have found that some of 1 are 100 times more active than tin catalysts usually employed such as dibutyltin dilaurate.[4]

In the course of our program on synthetic applications of organotin templates, we perceived that this unusual catalytic activity should be ascribed to the unique structure of 1 and started detailed investigations on the catalytic mechanism which should help delineate the reactivity features of 1.

There have appeared a number of proposals on the catalytic mechanism of organotin catalysts other than distannoxanes. Many authors have claimed that the ternary (tin–alcohol–isocyanate) complex is responsible for activation of the alcohol–isocyanate reaction.[5] Frisch and his co-workers have proposed the reaction between each reactant that is complexed with separate metals.[6] Davies and his co-workers have suggested the intermediacy of tin alkoxides which add to the isocyanate giving stannylcarbamates.[7] More recently, ionic intermediates such as $[Bu_2SnOCOC_{11}H_{23}]^{+}$[8] and $[Bu_2Sn(OAc)_2OMe]^{-}$[9] have been proposed as active species.

The present study stemmed from the expectation that the unique dimeric structure of distannoxanes should give rise to reactivities heretofore unknown, but characteristic of these compounds. Consequently, detailed investigation of the catalytic activity of various types of distannoxanes

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[1] Organotin Templates in Organic Reactions. 6.

[2] Okawara, R.; Wada, M. *Adv. Organomet. Chem.* **1967**, *5*, 137.

[3] Yano, T.; Nakashima, K.; Otera, J.; Okawara, R. *Organometallics* **1985**, *4*, 1501 and references cited therein.

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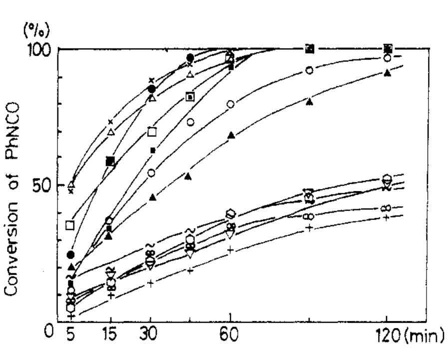


Figure 1. Time–conversion curve of phenyl isocyanate in the reaction with *n*-butyl alcohol catalyzed by organotin compounds (PhNCO:*n*-BuOH:catalyst = 1:1:5 × 10^{-5}): (○) **1a**; (▲) **1b**; (■) **1c**; (▽) **1d**; (○) **1e**; (●) **1f**; (△) **1g**; (×) **1h**; (□) **1i**; (+) **2a**; (~) **3a**; (∞) **3b**.

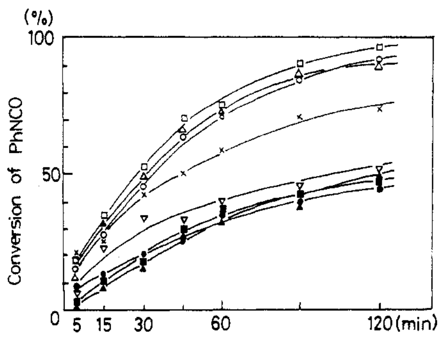


Figure 2. Time–conversion curve of phenyl isocyanate in the reaction with *n*-butyl alcohol catalyzed by distannoxanes (PhNCO:*n*-BuOH:catalyst = 1:1:3 × 10^{-5}): (▽) **1b**; (■) **1c**; (▲) **1e**; (●) **1f**; (×) **1g**; (△) **1h**; (○) **1i**; (□) **1j**.

in alcohol–isocyanate reactions have been undertaken. In this paper, the results will be discussed with the aid of ^{119}Sn NMR spectra since we have found that this spectroscopy is helpful in characterizing distannoxanes in solution.[3,10]

Results and Discussion

Catalytic activities of various organotin compounds for the reaction of 1-butanol and phenyl isocyanate in 1:1 molar ratio have been compared in terms of the reaction rate of the isocyanate.[4,11] Figure 1 illustrates the time–conversion curves with a catalyst concentration of 5 × 10^{-3} mol% relative to phenyl isocyanate. It is evident that distannoxanes except 1,3-dichloro and 1,3-dibromo derivatives are more active than Me_3SnOH (**2a**), Bu_3SnOMe (**3a**), and Bu_3SnOPh (**3b**). It should be recognized, however, that the activities of these trialkyltin compounds are superior to those of the usual tin catalysts such as dibutyltin dilaurate or stannous octoate.[4] In order to further differentiate these active distannoxanes, the reaction was conducted at the lower catalyst level (3 × 10^{-3} mol %). Figure 2 indicates that the catalysts may be classified into two groups. The distannoxanes containing an isothiocyanate group exhibit enhanced catalytic activity as compared with the corresponding halodistannoxanes. As a whole, the catalytic behavior of **1** depends on two major factors: (1) the presence of a hydroxy or alkoxy (phenoxy) substituent is effective to a considerable degree and (2) the isothiocyanate group is more effective in improving the activity.

Let us consider first the effect of a hydroxy substituent. It is crucial to determine whether a catalyst reacts initially with an alcohol or an isocyanate. Addition of 10 equiv of an alcohol to a CDCl$_3$ solution of **1b** and **1h** at room temperature immediately induced low field shifts of ^{119}Sn NMR signals of the distannoxanes. The results are summarized in Table I in which are listed δ (^{119}Sn) values of the corresponding alkoxides that were prepared separately. Apparently, newly formed species are attributable to the alkoxides. The facile formation of alkoxides was further confirmed by the following experiments: the hydroxydistannoxanes were dissolved in hot methanol, and when the solutions were kept at room temperature, crystallization of methoxydistannoxanes occurred quantitatively. On the other hand, addition of phenyl isocyanate to the CDCl$_3$ solution of these distannoxanes gave rise to unidentifiable complex signals suggestive of decomposition of the distannoxane structure.

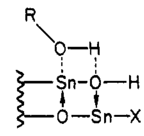
Table I. Comparison of ^{119}Sn Chemical Shifts [δ (^{119}Sn)] of Tetraorganodistannoxanes in the Absence or Presence of Alcohols (10 equiv) in CDCl$_3$

distannoxane	alcohol	δ
$ClBu_2SnOSnBu_2OH$		−158.6, −175.0
	MeOH	−155.0, −173.5
	$RhCH_2OH$	−150.3, −171.7
$SCNBu_2SnOSnBu_2OH$		−162.2, −211.8
	MeOH	−161.4, −208.5
$ClBu_2SnOSnBu_2OMe$		−155.4, −174.5
$ClBu_2SnOSnBu_2OCH_2Ph$		−151.2, −172.9
$SCNBu_2SnOSnBu_2OMe$		−161.4, −208.9

Next, the stoichiometric reaction of methanol and phenyl isocyanate was investigated in the presence of **1b**. An equimolar mixture of methanol and **1b** was stirred in benzene at room temperature for 1 h. Addition of phenyl isocyanate to this mixture afforded methyl *N*-phenylcarbamate in 95% yield. In contrast, addition of methanol to the equimolar mixture of phenyl isocyanate and **1b** which had been stirred in benzene at room temperature overnight led to little formation of methyl *N*-phenylcarbamate. Without doubt, the above results indicate that the catalytic reaction is initiated by the formation of the alkoxydistannoxane.

In contrast to other organotin compounds, distannoxanes are unique in that hydroxy derivatives are readily isolable. Of further interest is the facile alcoholysis of these hydroxy compounds. For example, few simple organotin hydroxides have been isolated on account of their tendency to condense into organotin oxides. The only exceptional compound that has been fully identified is trimethyltin hydroxide (**2a**).[12] However, this compound was found to resist to methanolysis in refluxing methanol. For **2a**, the oxygen-bridged polymeric structure in the solid state[12b] and the dimeric formulation in solution[12a] have been elucidated. Accordingly, the self-condensation of this compound as well as of hydroxydistannoxanes is viewed as being suppressed by the association.

The readiness to alcoholysis of hydroxydistannoxanes also is ascribable to the oxygen-bridged structure. That the reaction proceeds via a nucleophilic attack of an alcohol was confirmed by the treatment of **1b** with optically active 2-octanol.



Hydrolysis of the optically pure (1-methylheptoxy)dis-

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(10) A part of this study has appeared in preliminary form: Otera, J.; Yano, T.; Okawara, R. *Chem. Lett.* **1985**, 901.

(11) Ferstandig, L. L.; Scherrer, R. A. *J. Am. Chem. Soc.* **1959**, *81*, 4838.

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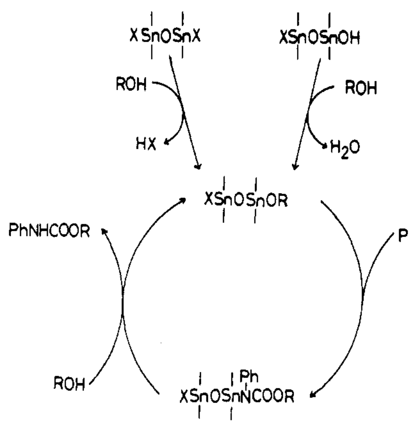
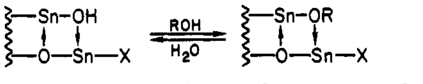
Scheme I

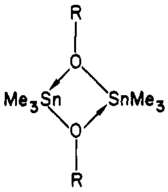


tannoxane resulted in complete retention of the optical purity of 2-octanol recovered, in support of no cleavage of the R–O bond. The nucleophilic attack of an alcohol should be favored by the hydroxy oxygen bridge in hydroxydistannoxanes because of the decrease in electron density of this bond. Then, why does **2a** resist to methanolysis despite its structural similarity to distannoxanes? The most probable explanations for the difference in reactivity of these two types of compounds are based on the thermodynamic stability of the resulting alkoxides. It is apparent that alcoholysis of hydroxydistannoxanes is an equilibrium reaction (eq 1) since the alkoxides regenerate



(1)

the hydroxides rapidly under hydrolytic conditions or gradually on exposure to air. Trimethyltin alkoxides (**2b**) which are to be formed if **2a** undergoes alcoholysis are far more sensitive to hydrolysis although these compounds are usually dimeric. However, we must consider that the

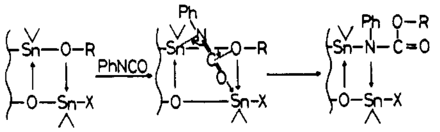


2b

coordination of the alkoxy group in **2b** is weaker than that in alkoxydistannoxanes since the coordinated tin in the latter compounds is bonded to an electronegative atom (halogen) or group (NCS). X-ray studies on hydroxydistannoxanes elucidated that the length of the coordinate Sn–O bond in the central four-membered ring was comparable to that of Sn–OH bond. Furthermore, ^{119}Sn NMR study has suggested a considerable covalency in the coordinated Sn–O bond.[3] This is why the distannoxanes undergo facile alcoholysis and the equilibrium deviates in favor of the hydroxide in trimethyltin derivatives. It is reasonably assumed that the alkoxydistannoxanes thus formed add to phenyl isocyanate by analogy with the reaction of trialkyltin alkoxides.[7] Alcoholysis of the resulting stannylcarbamate affords *N*-phenylcarbamate esters and regenerates the alkoxydistannoxanes (Scheme I).

As Figure 2 clearly shows, no difference was encountered in the catalytic activity between hydroxy- and alkoxy- (or phenoxy-) distannoxanes, a result which suggests that the initial reaction of hydroxydistannoxanes with alcohol is quite rapid as compared with the accompanying reactions. The intermediacy of the alkoxydistannoxanes is valid in the case of 1,3-dihalo- and 1,3-diisothiocyanatodistannoxanes as well since these compounds give methoxydistannoxanes simply on exposure to refluxing methanol. That the reaction proceeds in such a smooth manner is quite surprising. In general, organotin halides never react with alcohol even in the presence of a base. Recent X-ray analyses have revealed that the bridging chlorine in 1,3-dichlorotetraorganodistannoxanes is a chloride anion.[13] In addition, the highly polarizable nature of the Sn–NCS bond in distannoxanes has been proved on the basis of electric conductivity which is the subject of future discussion. The highly ionic or polarizable Sn–X (X = halogen, NCS) bond which should be sensitive to nucleophilic attack, along with the thermodynamic stability arising from the rigid $\overline{\text{Sn–O–Sn–OR}}$ ring formation seems to effect alcoholysis of 1,3-dihalo- or 1,3-diisothiocyanatodistannoxanes. Although an alkoxytin intermediate has been proposed for tin-catalyzed urethane formation,[7] the presence of the alkoxide in an actual catalytic system has not been proved. Therefore, the present study affords the first evidence for the alkoxide intermediate.

Scheme II



Next, the roles of the alkoxydistannoxanes in the catalysis will be discussed. As depicted in Scheme I, the catalytic cycle consists of a sequence of two reactions: addition of alkoxydistannoxanes to an isocyanate (step 1) and alcoholysis of the resulting stannylcarbamates (step 2). Figure 1 shows that methoxy- or phenoxydistannoxanes are more active than tributyltin methoxide or phenoxide. Reactivities of the stannylcarbamates derived from these two types of compounds in step 2 are comparable since an Sn–N bond, in general, is highly susceptible to alcoholysis.[14] Therefore, the unique activity of distannoxanes is ascribed to an enhanced reactivity of the Sn–OR bond in these compounds toward isocyanate (step 1) probably due to the activation of the Sn–OR bond caused by the alkoxy bridge as already discussed for hydroxydistannoxanes. Moreover, the reaction is accelerated by the coordination of isocyanate to tin as shown in Scheme II. Possibly, the coordination occurs on the tin attached to X (X = halogen or NCS) rather than that attached to an alkoxy group because diorganotin halides or pseudohalides readily furnish donor–acceptor complexes whereas only a few adducts of organotin alkoxides are known. In other words, there exists the template effect by which an addition reaction of isocyanate occurring at the tin attached to an alkoxy group is accelerated by the tin of the other chain. This is consistent with the result that the catalytic activity is dependent on X. In order to account for the effect of X, the Sn–X bond was characterized by means of electric conductivity. Molar conductivities of **1b** and **1h** in Me$_2$SO solution (10^{-3} mol/L) were found to be 6.36 and 24.6 s·cm^2·mol^{-1}, respectively. The value for the latter compound nearly corresponds to that of a 1:1 electrolyte since a Me$_2$SO solution (10^{-3} mol/L) of KI gave rise to a molar conductivity of 47.6 s·cm^2·mol^{-1}. Apparently, an Sn–X bond is polarized on coordination of a donor molecule to tin. Especially, the highly polarizable nature of the Sn–NCS bond allows isocyanate to coordinate to tin with much ease. The facile methanolysis of the bridging Sn–NCS

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[14] Jones, K.; Lappert, M. F. *Organotin Compounds*; Sawyer, A. K., Ed.; Marcel Dekker: New York, 1972; Vol. 2, p 509.

bond in the 1,3-diisothiocyanato derivative as described before is thus attributed to the polarizability of this bond.

In conclusion, the mechanistic investigation of the urethane formation catalyzed by 1,3-disubstituted tetrabutyldistannoxanes revealed various reactivity profiles of these compounds. (1) The bridging hydroxy group and (pseudo)halogen are cleaved by alcohol under mild reaction conditions. The analogous reaction never occurs with other organotin compounds. (2) Another notable feature is the unusual ease with which the Sn–OR bond in alkoxydistannoxanes undergoes a nucleophilic attack. Both of these reactions can be associated with activation of the tin–heteroatom bond through coordination. (3) Moreover, the considerably acidic tin located in the proximity of the reaction site failitates the reaction of isocyanate with the Sn–OR bond.

Among expanding synthetic application of organotin compounds, efficient manipulation of an Sn–OR bond is pivotal to mild esterification.[15] The above findings prompt us to expect that alkoxydistannoxanes may provide various synthetic use which has not been uncovered with other metal alkoxides yet. The studies along this line will be published in due course.

Experimental Section

^{119}Sn NMR spectra with complete proton noise decoupling were obtained by using a JEOL FX-100 spectrometer operating at 37.08 MHz. Field frequency control was made with a deuterium-labeled solvent ($CDCl_3$) lock. The chemical shifts were determined relative to internal Me_4Sn, negative signs indicating high-field shifts from the reference. Electric conductivity was measured with a Toa Denpa Ind. CM-15A digital conductivity meter. Measurements of $[\alpha]_D$ were carried out with a Union Giken PM-101 automatic digital polarimeter.

Solvents were purified by standard methods. Preparation of distannoxanes was described previously.[3] Optically active (*R*)-(–)-2-octanol was purchased from Nakarai Chemicals Ltd. The rate of the 1-butanol–phenyl isocyanate reaction was followed by the amine equivalent method.[4,11]

Reaction of Methanol with Phenyl Isocyanate in the Presence of 1b. A benzene solution (10 mL) containing methanol (45 mg, 1.4 mmol) and **1b** (746 mg, 1.4 mmol) was stirred at room temperature for 1 h. To this solution was added phenyl isocyanate (167 mg, 1.4 mmol). After being stirred for 1 h, the reaction mixture was evaporated. Column chromatography of the residue on silica gel (10:1 hexane–ethyl acetate) afforded methyl *N*-phenylcarbamate (201 mg, 95%), which was identified by comparison with an authentic sample.

Reaction of 1,3-Dihalo- and 1,3-Diisothiocyanatodistannoxanes with Methanol. A methanol solution (15 mL) of **1g** (299 mg, 0.5 mmol) was heated at reflux for 2 h. Methanol was evaporated, and the residue was found to consist of **1g** and **1j** in 18:82 ratio. 1,3-Dibromo and 1,3-dichloro derivatives afforded a mixture of the starting material and the methoxydistannoxane in 70:30 and 95:5 ratios, respectively.

Hydrolysis of Optically Active (1-Methylheptoxy)distannoxane. A benzene solution (30 mL) of **1b** (2.926 g, 5.48 mmol) and (*R*)-(–)-2-octanol ($[\alpha]_D$ –8.76 (*c* 5.575, EtOH); 0.713 g, 5.48 mmol) was heated with a Dean-Stark apparatus to remove water for 6 h. Removal of benzene yielded oily (1-methylheptoxy)distannoxane, which was then treated with 1 N HCl/methanol. Extraction of the mixture with ether afforded (*R*)-(–)-2-octanol (0.639 g, 89.4%; $[\alpha]_D$ –8.82 (*c* 5.575, EtOH)).

Acknowledgment. Thanks are due to Prof. H. Nozaki for helpful discussions.

Registry No. **1a**, 33194-92-2; **1b**, 95970-99-3; **1c**, 95971-00-9; **1d**, 33335-94-3; **1e**, 95971-01-0; **1f**, 95971-02-1; **1g**, 95971-03-2; **1h**, 95971-04-3; **1i**, 95971-05-4; **1j**, 101224-52-6; 1 (R = Bu, X = 1-methylheptoxy, Y = Cl), 101224-53-7; **2a**, 56-24-6; **3a**, 1067-52-3; **3b**, 3587-18-6; PhNCO, 103-71-9; *n*-BuOH, 71-36-3; MeOH, 67-56-1; PhNHCOO-*n*-Bu, 1538-74-5; PhNHCOOMe, 2603-10-3; (*R*)-(-)-2-octanol, 5978-70-1.

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(15) David, S.; Hanessian, S. *Tetrahedron* **1985**, *41*, 634.