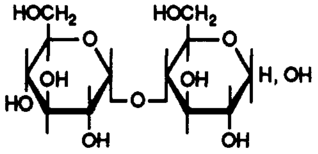
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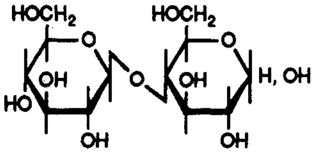
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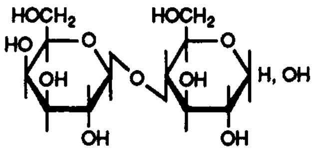
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summarized in Table I. It is seen from Table I that these saccharides from 1:1 complexes with 2 and the θ_{max} values are correlated with the K values: the larger the θ_{max}, the greater the K.

Why does only 2 afford the CD-active complexes? Compound 1 should also form complexes with saccharides, but they are all CD silent. Compound 2 can form a cyclic structure through the two-site binding (as shown in Figure 2). Conceivably, the ring structure would freeze the molecular motion of chromophoric benzene moieties in 2. This situation is favorable for the appearance of a CD band.[18] The explanation is compatible with the fact that the complexes with disaccharides, the rings of which are more flexible because of a central ether linkage, result in the smaller K values.

In conclusion, we believe that the present CD spectroscopic method serves as a new, promising sensory system for sugar molecules. Particularly, the finding that the CD spectrum is observed only when the ring-structured molecular models can be made is useful for predicting the configuration of sugar molecules.

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Supplementary Material Available: Experimental procedures for the preparation of 1 and 2 and the determination of association constants (2 pages). Ordering information is given on any current masthead page.

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Sn(OTf)$_2$-Promoted Addition of 1-Alkynes to Aldehydes

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Summary: 1-Alkynes add to aldehydes and ketones in the presence of Sn(OTf)$_2$ and an amine giving acetylenic alcohols in high yields.

The addition of metal acetylides to aldehydes is one of the most important transformations in organic synthesis, and alkali or alkali-earth metal derivatives have been generally employed for this purpose.[1] The basic nature of these reagents and the requirement of strong bases such as alkylmetals or metal amides for their generation, however, sometimes causes base-induced side reactions. In order to overcome these problems, several improved methods have been developed. For example, B,[2] Al,[3] Ce,[4] V,[5] and Mn[6] acetylides, which have been generated by transmetalation of Li, Na, or Mg acetylides, add to aldehydes and ketones. The addition reactions of Si[7] and Sn derivatives[8] were conducted in the presence of a Lewis acid or fluoride ion. 1-Haloalkynes have been added to aldehydes in the presence of CrCl$_2$.[9] Although the acetylide addition reaction can be achieved under milder conditions by these methods, the process is often not straightforward. If reactive metal acetylides could be formed from 1-alkynes with amine bases, such a method would provide a novel and useful synthetic tool. In fact, copper or palladium acetylides have been generated with amine bases,[10] although these species are not reactive enough to add to aldehydes.[11] It seemed to us that the proper selection of a metal salt in combination with an amine base might allow generation of metal acetylides that are reactive enough to add to C═O bonds. We have found

Scheme I

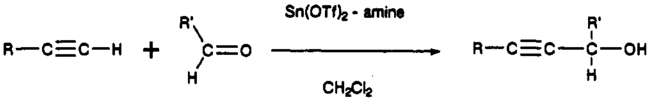

Table I. The Addition of 1-Alkynes to Aldehydes Promoted by Sn(OTf)$_2$ and Amines

R	aldehyde	method[a]	yield[b] (%)
Ph	c-C_6H_{11}	A	87, 74,[c] 70[d]
	t-BuCHO	A	81
	n-C_4H_9CHO	A	66
	PhCHO	A	66
	$PhCH_2CH_2CHO$	A	86
p-$MeOC_6H_4$	c-C_6H_{11}	A	91
PhCH═CH	c-C_6H_{11}	A	82
$PhCH_2CH_2$	t-BuCHO	B	64
	n-C_4H_9CHO	C	89
	$PhCH_2CH_2CHO$	C	71
n-C_5H_{11}	c-C_6H_{11}	B	76
	t-BuCHO	B	70
	$PhCH_2CH_2CHO$	C	57

[a] The reactions were carried out with Sn(OTf)$_2$ (1 mmol), amine (1 mmol), 1-alkyne (1 mmol), and aldehyde (0.33 mmol) by method A, B, or C (see text), unless otherwise noted. [b] Isolated yields are shown. All new compounds gave satisfactory ^{1}H NMR ^{13}C NMR, and IR spectra are elementary analyses either by HRMS or combustion. [c] The reaction was carried out with 15 mmol of the nucleophile and 5 mmol of aldehyde. [d] Two equivalents of the nucleophile was used.

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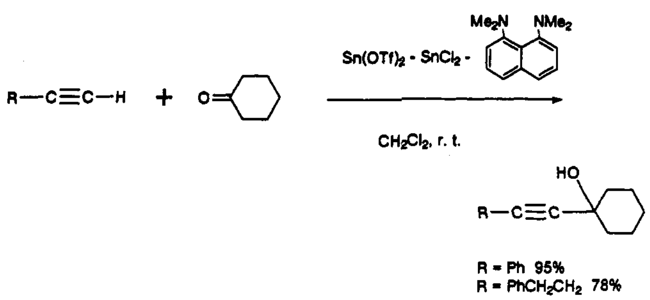
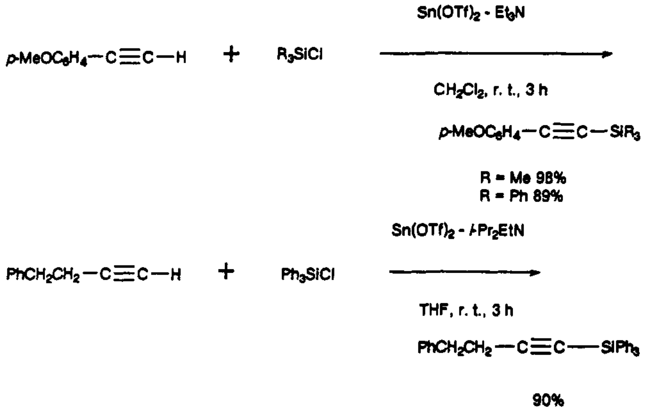
Scheme II



Scheme III



that Mukaiyama's $Sn(OTf)_2$ reagent[12] works efficiently for this purpose (Scheme I).

When a 1-alkyne (3 equiv) is treated with $Sn(OTf)_2$ (3 equiv) and an amine (3 equiv) in CH_2Cl_2 followed by an aldehyde (1 equiv), the addition reaction took place smoothly at rt giving an acetylenic alcohol in good yield (Table I). The reaction can be applied to both aromatic alkynes and aliphatic alkynes with a slight modification of the reaction conditions: The use of DBU (method A) gave the adducts in higher yields in the former reactions, and 1,8-bis(dimethylamino)naphthalene (method B) in the latter. The addition of aliphatic alkynes to aldehydes that readily undergo aldol reaction was carried out with a $Sn(OTf)_2$–$SnCl_2$[13] mixture (method C) in the presence of 1,8-bis(dimethylamino)naphthalene. The reaction can be applied to ketones as exemplified by cyclohexanone (Scheme II). More hindered ketones such as diisobutyl ketone or diisopropyl ketone, however, did not react.

The synthesis of 1-cyclohexyl-3-phenyl-2-propyn-1-ol typifies the procedure: Under a nitrogen atmosphere, DBU (2.24 mL, 15 mmol) was added to $Sn(OTf)_2$ (6.26 g, 15 mmol) and phenylacetylene (1.53 g, 15 mmol) in CH_2Cl_2 (20 mL), and the mixture was stirred at rt for 10 min. A CH_2Cl_2 (5 mL) solution of cyclohexanecarbaldehyde (0.56 g, 5 mmol) was added, and stirring was continued for 3 h at the same temperature. The reaction was quenched by adding 2 N HCl, and the adduct (0.79 g, 74%) was obtained by a standard workup.

Although the precise mechanism of this rection remains unclear, the formation of a nucleophilic organometalic species such as a Sn acetylide as the reactive intermediate is possible. In addition, silylation of 1-alkynes with a silyl chloride could be effected with the $Sn(OTf)_2$-amine promoter (Scheme III).

Further synthetic applications of this chemistry are now in progress.

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