Tetrahedron Letters No. 31, pp 2847 - 2850.
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0040-4039/78/0729-2847$02.00/0

A HIGHLY STEREOSELECTIVE C-C COUPLING OF ALDEHYDES FORMING GLYCOLS VIA A STANNYLENOID REACTION

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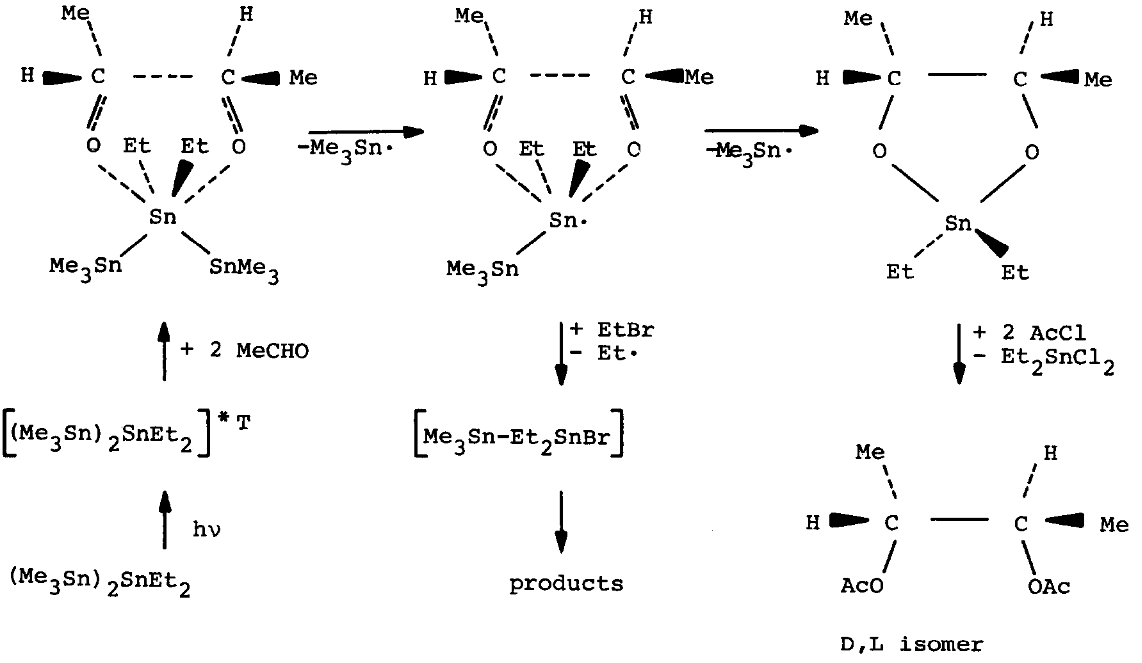
(Received in UK 22 May 1978; accepted for publication 2 June 1978)

The formation of 2-stanna-1,3-dioxolanes from aldehydes [4] is found to be highly stereoselective, if proper stannylene precursors are used, see table 1. The mechanism is illustrated by the following tristannane. There is evidence for a stannylenoid mechanism, starting from a relatively longlived triplet state [5]:



The radical scavengers BuCl and iPrCl, trapping all diffusing stannyl radicals, are without influence on this reaction. Therefore, no free radicals are involved in what happens with the aldehyde. The strong scavenger EtBr, however, penetrating into solvent cages, attacks the reactive intermediate giving Me_3SnBr + Et_2SnBr_2, and prevents the formation of the stannadioxolane.

Table 1. Stereoselectivity of the reaction of $R_2SnR'R"$ with acetaldehyde,[a)] estimated by g.l.c. of the resulting butane-2,3-diacetate.

$R_2SnR'R"$			Overall	
R	R'	R"	yield, %[b)]	D,L isomer, %
Me	$PhCH_2$	$PhCH_2$	42	91
Me	Me	Me_3Sn	70	89
Et	Et	Et_3Sn	70	96
Bu	Bu	Bu_3Sn	70	100
Me	Cl	Me_2ClSn[c)]	74	58
Et	Br	Et_3Sn	21	96
Me	Me_3Sn	Me_3Sn	72	70
Et	Me_3Sn	Me_3Sn	77	94
Bu	$(-Bu_2Sn)_5$		$\geqq$ 22	100

a) molar ratio about 1:10, in benzene or n-hexane, at room temperature. Irradiation with a high pressure mercury arc.

b) not optimized.

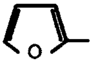
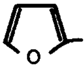
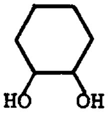
c) the corresponding stanna-dioxolane contains a methyl chlorotin moiety.

In all cases the stanna-dioxolane has been isolated, identified by IR and elemental analysis, and then converted to the butane-2,3-diacetate by acetyl chloride, which reacts exothermally.

High steric requirements of the reactive intermediate as a condition for the stereoselectivity of the C-C coupling can be concluded from the hexaalkyl distannane series (% D,L isomer) Me 89 < Et 96 < Bu 100.

A variety of aldehydes including α,ω-dialdehydes can be used for this new synthesis, mostly giving products with high D,L content. Tristannanes or cyclostannanes are found to be good stannylene precursors for preparative use, see table 2.

Table 2. Glycols from a variety of aldehydes

Aldehyde R-CHO	Stannylene precursor	Product	Yield[a]	Stereoselectivity
Me	Me_8Sn_3	$(MeCHOH)_2$	72	70% D,L
Et	Me_8Sn_3	$(EtCHOH)_2$	50	96% D,L
Pr	Me_8Sn_3	$(PrCHOH)_2$	64	88% D,L
Ph	Me_8Sn_3	$(PhCHOH)_2$	15	91% D,L
Ph	$(Bu_2Sn)_6$	$(PhCHOH)_2$	39	92% meso
	Me_8Sn_3	 $-CHOH)_2$	59	66%/34% [b]
$(-CH_2-CH_2-CHO)_2$	Me_8Sn_3		59	73% trans

a) not optimized.

b) the two isomers are not identified, at present.

Other glycol preparations from aldehydes are, in general, not stereoselective, with several exceptions: meso-hydrobenzoines have been prepared electrochemically from hydroxybenzaldehydes.[8] Using titanium reagents, the unspecific dimerization of ketyls could be transformed to a stereoselective olefin synthesis, passing intermediate diols.[9]

Procedure. In typical experiments, 20 mmol of the aldehyde are irradiated with 2 mmol of Me_8Sn_3 in 2 ml benzene with a high pressure mercury arc. After removing the liquid parts by filtration or centrifugation, the residue is washed several times with benzene. An excess of MeCOCl is added with n-hexane as diluent, and the easily volatile parts are evaporated in vacuo. The residue is dissolved in n-hexane and fractionated by g.l.c.. In the case of adipindialdehyde, 10 mmol are used, and 5 ml of Me_3SiCl instead of MeCOCl. With furfural, also the silyl ethers were used to separate the isomeric glycols. All experiments were carried out under dry argon.

Ketones, e.g. acetone, give poor yields or do not react at all, probably because of their lower carbonyl activity and higher steric hindrance in the reactive intermediate.

We are investigating now the application of this synthesis to natural products or precursors thereof.

Acknowledgement. We are grateful to the Deutsche Forschungsgemeinschaft for support, to the Schering AG for organotin starting materials, and to the Fonds der Chemischen Industrie for valuable substances.

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5. Upon UV-irradiation in solution without a partner, the tristannane shows ^{119}Sn-CIDNP effects, all three tin atoms giving enhanced absorption, even with the strong radical scavenger EtBr as solvent. An excited triplet state has to be concluded.[6]
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