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A SIMPLE, STEREOSELECTIVE, ROOM-TEMPERATURE SYNTHESIS OF CIS VINYLOXIRANES AND TRANS 1-PHENYL-1,3-BUTADIENE

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Summary : The organotin reagent from 1-chloro-3-iodoprop-1-ene and $SnCl_2$ in dimethylformamide reacted with aldehydes by its chlorine-substituted carbon atom. Treatment with NaOMe then gave cis vinyloxiranes with good stereoselectivity. Benzaldehyde and 1-bromo-3-iodoprop-1-ene in the presence of two equivalents of $SnCl_2$ gave exclusively trans 1-phenyl-1,3-butadiene.

Vinyloxiranes with defined configurations are attractive precursors of functionnalized four-carbon sequences. Furthermore, they may be alkylated by CH acids in the presence of Pd(0) catalysts,[1] leading to a variety of products. Many recent syntheses end with modernized versions of the elimination of a leaving group vicinal to a hydroxy function. The difficulties lie in the stereoselective building of the precursor. To this end, functionnalized allyl lithium derivatives were prepared and condensed with aldehydes and ketones, either as such,[2] or after modification by the addition of CdI_2,[3] Et_3Al,[4] titanum isopropoxide,[5] and other various additives,[6] sometimes in a highly stereoselective manner.[7] On the other hand, our approach, described in this letter, takes advantage of the known reactivity of allyltin compounds. These are most easily prepared from stannous halides by an insertion reaction, and it has been demonstrated that a reagent prepared from allyl iodide and SnF_2 reacts efficiently with carbonyl derivatives in the solvent 1,3-dimethyl-2-imidazolidinone.[10] The following experiments were run with the easily available reagent, anhydrous stannous chloride, in the solvent dimethylformamide at room temperature, and simply chlorine or bromine atoms as leaving groups.

Experimental

Commercial 1,3-dichloro- and 1,3-dibromopropenes were converted respectively to 1-chloro-3-iodo- and 1-bromo-3-iodoprop-1-enes with NaI in acetone. Stannous chloride was used as a concentrated solution in dimethylformamide (600 g/l). All experiments were performed at room temperature under nitrogen.

Vinyloxiranes. 1-Chloro-3-iodoprop-1-ene (E, Z, 35:65) (1 eq.) was added to the $SnCl_2$ solution (1.05 eq. of $SnCl_2$). After 15 min, the aldehyde (0.8 eq.) was added and the mixture was kept for 16 hours. After a two-phase isolation with CH_2Cl_2 as extractant, 2 M NaOMe in MeOH was added (2 eq.). The products were finally separated by HPLC (silica gel; hexane-EtOAc).

1-Phenyl-1,3-butadiene. The method was the same, except for the use of 1-bromo-3-iodoprop-1-ene with two equivalents of $SnCl_2$ and the absence of methoxide treatment.

Table I. Syntheses of vinyloxiranes according to equation (1).

	Chlorohydrin		Oxirane		
	Major %	Minor %	cis %	trans %	Isolated yield
Ph	89	11	89	11	53
$PhCH_2CH_2$			78	22	52
$CH_3(CH_2)_6$			74	26	51
(E)PhCH=CH			89	11	51

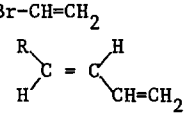
Discussion

Identification of oxiranes (Table I) rested on their ^1H NMR spectra (Table II), accepting the reported[11] ^3J values, 2 and 4 Hz for vicinal coupling in trans and cis oxiranes. Reaction (I) is most likely :

(1) $RCHO + ClH{=}CH{-}CH_2I + SnCl_2 \longrightarrow R{-}CH(OSnCl_2I){-}CHCl{-}CH{=}CH_2 \xrightarrow{MeO^-}$

Trans 1-substituted 1,3-butadienes were always isolated as side products (Table II). We suspected that they originated from a double stannylation followed by a Petersen-like elimination :

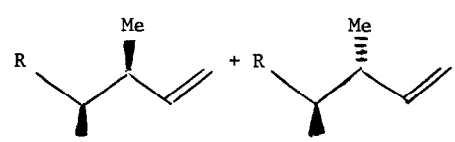
(2) $RCHO + BrCH{=}CH{-}CH_2I \xrightarrow{SnCl_2} R{-}CH(OSnCl_2I){-}CHBr{-}CH{=}CH_2$

$\xrightarrow{SnCl_2} R{-}CH(OSnCl_2I){-}CH(SnCl_2Br){-}CH{=}CH_2 \longrightarrow$ 

Accordingly, benzaldehyde reacted with $BrCH{=}CH{-}CH_2I$ in the presence of two equivalents of $SnCl_2$ to give the homogeneous trans 1-phenyl-1,3-butadiene in 54% yield (Table II, cf[12]).

The oxiranes, dienes, together with starting materials were the only products, which were not highly polar. No unrearranged allylic product was observed, as is the rule with allyltin and silicon reagents.[13] To gain further insight into the nature of the intermediate we examined the similar reaction of crotyl bromide :

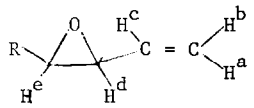
(3) $R{-}CHO + CH_3{-}CH{=}CH{-}CH_2Br \xrightarrow{SnCl_2}$



syn anti

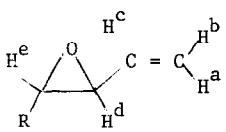
Table II. ^{1}H NMR Parameters of Vinyloxiranes and trans-Butadienes.

cis-Epoxides



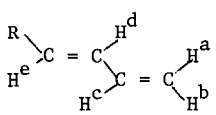
R	a	b	c	d	e	Others
Ph*			(6.9)	3.60 (4.2)	4.16	δ 7.3 (Ph)
Ph-CH_2-$\overset{f}{C}H_2$	5.40 (17)	5.27 (10.2)	5.63 (6.8)	3.35 (4.3)	3.06 (6.3)	δ ∿1.80 (CH_2), ∿7.2 (Ph) J_{ab} 1.8 Hz
CH_3-$(CH_2)_6$	5.45 (17)	5.33 (10.2)	5.71 (7)	3.39 (4.3)	3.07 (4.5)	δ 2.30 (Me), J_{ab} 2 Hz
Ph, H^g>C = C<H^f	5.49 (17.5)	5.33 (10.5)	5.76 (7)	3.56 (4)	3.64 (7.5)	δ 6.02 (H^f), 6.73 (H^g) ∿7.4 (Ph) J_{fg} 16 Hz

trans-Epoxides



Ph*				3.30	3.71	δ ∿7.3 (Ph)
Ph-CH_2-$\overset{f}{C}H_2$	5.35 (17)	5.18 (10)	5.40 (7)	3.01 (2)	2.91 (7.5)	δ ∿ 1.8 (CH_2), 7.2 (Ph) J_{ab} 2 Hz
Ph, H^g>C = C<H^f	5.52 (17)	5.30 (10)	5.57 (7)	3.36 (2)	3.41 (7.5)	δ 5.93 (H^f), 6.76 (H^g), J_{fg} 16 Hz

trans-Butadiènes



Ph**	5.25 (16.5)	5.10 (10.5)	6.42 (10.5)	6.72 (15.5)	6.46	Aromatic H's : δ 7.29 (H_o), 7.19 (H_m), 7.16 (H_p); J_{cp} = J_{cm} = 7.5
Ph-$\overset{g}{C}H_2$-$\overset{f}{C}H_2$	5.09 (17)	4.96 (10)	6.29 (10)	6.08 (14.8)	5.72 (7.4)	δ 2.40 (H^f), 2.69 (H^g)

The ^{1}H NMR spectra were determined at 250 MHz for samples dissolved in $CDCl_3$ with Me_4Si as reference. In columns a-e, ^3J couplings to the protons next in alphabetical order are given in brackets beneath the chemical shift. *90 MHz spectrum. **400 MHz spectrum.

The syn : anti ratios were determined with the help of ^{1}H NMR parameters reported for similar sequences.[15] We observed good overall yields (51-68%), a moderate anti selectivity (34 : 66 at best), and exclusive 1,2-addition on cinnamaldehyde, with conservation of the E configuration. The same was true of the reaction of allyl iodide with crotonaldehyde (40%).[16]

Now coming back to equation (1), we expect the cis : trans ratios in oxiranes to reflect the syn : anti ratios in the chloro-carbinols. NMR examination of this intermediate (R = Ph) indicated a 89:11 diastereomeric mixture, the same ratio as in oxiranes. The major one is most likely the syn isomer, thus the selectivity is opposite to that of eq. (3).

The mechanisms of similar reactions appear to be still a matter of investigations. In our case, it would seem that the orientation of the carbon-halogen bond gauche to the carbon-oxygen bond is preferred in the transition state. The E configurations of the dienes are opposite to the favoured ones for the oxiranes. This is probably a consequence of the second step, which may be a Sn-O syn elimination.

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16. ^{1}H NMR Spectra of allylcarbinols (250 MHz, $CDCl_3$, Me_4Si) (Protons are numbered from the vinyl end with 1'-H as the proton cis to 2-H).
PhCHOH-CHCl-CH=CH_2 (major) : δ 4.42 (3-H), 4.60 (4-H), 4.99 (1'-H), 5.02 (1-H), 5.70 (2-H), 7.0 (OH), $J_{1,2}$ 16.8, $J_{1',2}$ 10, $J_{2,3}$ 7.3, $J_{3,4}$ 6.7 Hz; (minor) : δ 4.82 (4-H), $J_{3,4}$ 5.25 Hz.
CH_3-CH=CH-CHOH-CH_2-CH=CH_2 : δ 1.70 (Me), 2.25 (3-H), 2.30 (OH), 4.09 (4-H), 5.08 (1'-H), 5.09 (1-H), 5.41 (5-H), 5.66 (6-H), $J_{1,2}$ 16.5, $J_{1',2}$ 10.5, $J_{2,3}$ 7, $J_{3,4}$ 6.5, $J_{4,5}$ 6.5, $J_{5,6}$ 15, $J_{6,Me}$ 6 Hz.
PhCHOH-CHMe-CH=CH_2 : (anti) δ 0.84 (Me), 2.30 (OH), ∿2.50 (3-H), 4.32 (4-H), 5.14 (1'-H), 5.15 (1-H), 5.76 (2-H), $J_{1,2}$ 17, $J_{1',2}$ 10.5, $J_{2,3}$ 8, $J_{3,4}$ 6.8, $J_{Me,3}$ 7 Hz; (syn) δ 1.00 (Me), 2.3 (OH), 2.50 (3-H), 4.55 (4-H), 5.03 (1-H), 5.04 (1'-H), 5.71 (2-H), ca 7.2 (Ph), $J_{1',2}$ 10.5, $J_{2,3}$ 7, $J_{3,4}$ 5.7, $J_{4,Me}$ 7, $J_{1,2}$ 15 Hz.
PhCH=CH-CHOH-CHMe-CH=CH_2 (anti) : δ 1.03 (Me), 2.28 (OH), 2.32 (3-H), 4.00 (4-H), 5.12 (1'-H), 5.13 (1-H), 5.78 (2-H), 6.15 (5-H), 6.54 (6-H), ca 7.2 (Ph), $J_{1,2}$ 17.5, $J_{1',2}$ 10, $J_{2,3}$ 8, $J_{3,4}$ 6.9, $J_{3,Me}$ 6.5; $J_{4,5}$ 6.9, $J_{5,6}$ 16; (syn) : δ 1.05 (Me), 2.40 (3-H), 4.13 (4-H), 5.08 (1'-H), 5.09 (1-H), 5.81 (2-H), 6.16 (5-H), 6.53 (6-H), ca 7.2 (Ph), $J_{1,2}$ 15.5, $J_{1',2}$ 10, $J_{2,3}$ 7.5, $J_{3,4}$ 6, $J_{3,Me}$6,5, $J_{4,5}$ 6.9, $J_{5,6}$ 16 Hz.

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