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DIVALENT TIN-MEDIATED SYNTHESIS : A VERY SIMPLE, STEREOSELECTIVE ROUTE TO TERMINAL CONJUGATED (E) DIENES AND TRIENES.

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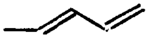
Summary : The conversion of aldehydes RCHO into terminal conjugated dienes $RCH{=}CH{-}CH{=}CH_2$ with (E) stereochemistry was carried out at room temperature with 1-bromo-3-iodopropene in the presence of $SnCl_2$. Starting from an unsaturated aldehyde, a terminal conjugated triene was obtained in the same conditions.

The stereocontrolled synthesis of conjugated dienes and trienes[1,2] is a major problem in organic and natural product chemistry : dienes are starting materials in the Diels Alder reaction; the elaboration of dienic and trienic systems with high isomeric purity remains a permanent problem in insect pheromone and leukotriene chemistry.

In a previous paper[3] we reported a new preparation of (E) 1-phenyl-1,3-butadiene from benzaldehyde. In this letter, we describe experiments which prove the general character of the new reaction (1) :

(1) $RCHO + BrCH{=}CH{-}CH_2I + 2\ SnCl_2 \longrightarrow$ R 

This is an extremely convenient reaction, since it works at room temperature with unsophisticated reagents. Furthermore, reaction (1) is stereoselective, since (E) dienes are obtained[4] from a mixture of (E) and (Z) dihalopropenes. Reaction (1) is regioselective, and also chemoselective.

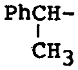
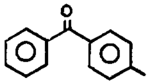
Experimental

1-Bromo-3-iodopropene was prepared from 1,3-dibromopropene by a conventional procedure.[5] Aldehydes, except the keto aldehyde[6], were purchased.

The following conditions for the preparation of phenylbutadiene may be considered as typical for dienes and trienes.

1-Bromo-3-iodopropene (5.3 mmoles; 1.3 g) was added to a solution of $SnCl_2$ (49.9 mmoles; 9.47 g) in DMF-toluene (6 + 6 ml). After 15 min, benzaldehyde (4.08 mmoles, 0.433 g) was added and the mixture was stirred overnight at room temperature. The mixture was then filtered on silicagel (about 35 g), with hexane as eluent; after evaporation of the solvent, (E) 1-phenyl-1,3-butadiene was distilled (0.328 g; 62%).

Table I. Synthesis $RCHO \longrightarrow RCH{=}CH{-}CH{=}CH_2$ (E)

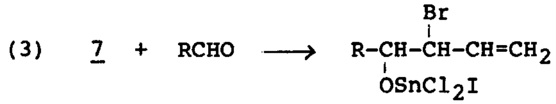
Diene or triene	R-	Isolated yield	References
1	Ph-	62	3, 7, 8
2	$Ph(CH_2)_2-$	67	3, 9
3	PhCH=CH-	70	10, 11
4	$CH_3-(CH_2)_7-$	45	12, 13
5	 $PhCH(CH_3)-$	40	14
6		57	

All the products, except 6 which was purified by hplc, were distilled under vacuum; yields were calculated after distillation (an evaluation by gc gave a 80% yield for 2). The (E) structure of dienes was assigned by 250 or 400 MHz proton NMR (J_{trans}= 15-16 Hz). Triene 3 was found pure by gc and ^{13}C NMR; the (E,E) structure was assigned from the UV and IR spectra : UV (ethanol) : 301 (39000), 313 (48000), 328 (36500) nm; IR (nujol) 1002, 967, 898, 747, 690 cm^{-1}. Diene 6 is a new compound with correct elementary analysis; UV spectrum (ethanol) : 242 (14200), 256 (13500), 318 (27400) nm; IR spectrum (nujol) : 1660, 1605, 1580, 1005, 950, 940, 925, 875 cm^{-1}.

Discussion.

It is known[15] that the insertion of stannous chloride into the carbon - iodine bond of allyl iodide leads to allylstannanes which react in situ with aldehydes to yield homoallylic alcohols. In our case (reactions (2) and (3)) this insertion should give first functionnalized allylstannanes[16] which react rapidly with aldehydes. We have indications that the limiting step is the oxidative addition[17] (2) :

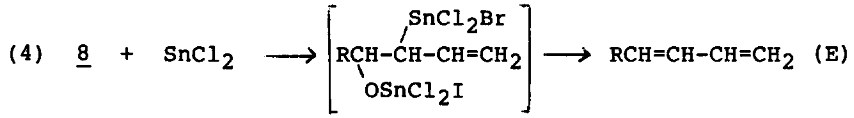
(2) $BrCH{=}CH{-}CH_2I + SnCl_2 \longrightarrow \underset{7}{BrCH{=}CH{-}CH_2SnCl_2I}$



$$(3)\quad \underline{7} + RCHO \longrightarrow \underset{\displaystyle OSnCl_2I}{R-CH}-\overset{\displaystyle Br}{CH}-CH=CH_2$$

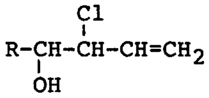
<u>8</u>

If there is an excess of $SnCl_2$, we postulate that a new insertion into the carbon-bromine bond of an allylic system occurs, followed by an elimination.



$$(4)\quad \underline{8} + SnCl_2 \longrightarrow \left[\underset{\displaystyle \backslash OSnCl_2I}{RCH}-\overset{\displaystyle /SnCl_2Br}{CH}-CH=CH_2 \right] \longrightarrow RCH=CH-CH=CH_2\ (E)$$

Such an elimination which is reminiscent of Peterson elimination in silicon chemistry was reported in tin chemistry in somewhat different cases.[19] Our reaction works with other 1,3-dihalopropenes such as 1-chloro-3-iodopropene and 1,3-dibromopropene; the yields are lower[20] but the (E) stereochemistry of dienes is unchanged. When 1-chloro-3-iodopropene is used, the intermediate, after hydrolysis, is <u>9</u> :

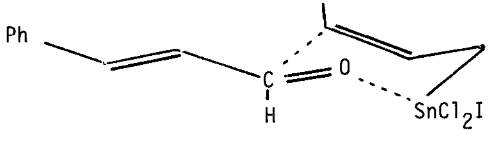


$$\underset{\displaystyle OH}{R-CH}-\overset{\displaystyle Cl}{CH}-CH=CH_2$$

<u>9</u>

<u>9</u> is a syn-anti mixture; the diastereomeric excess is 78% or less.[3] Since the diene obtained after insertion and elimination is always more than 95% pure,[4] any reaction mechanism should explain this improvement of stereoselectivity during the process.

The regioselectivity is an another advantage of this reaction. The nucleophilic site of <u>7</u> is exclusively the carbon linked to bromine. When an α,β-ethylenic aldehyde was used, the electrophilic site was exclusively the carbon linked to oxygen. The stereochemistry of the ethylenic double bond was not affected during the reaction : starting from (E) cinnamaldehyde, a pure (E,E) triene was obtained. These results agree with the suggestion that the transition state leading to <u>8</u> (R:-CH=CH-Ph) is a six-membered chair transition state :



The carbonyl function becomes more electrophilic by coordination with tin. This explains that the reaction proceeds without acidic catalyst.[21] In these conditions, ketones less electrophilic than aldehydes are completely inert. The chemoselectivity is total with the keto aldehyde leading to the diene <u>6</u>.

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3. J. Augé and S. David, Tetrahedron Lett., 24, 4009 (1983).
4. Dienes are analyzed by gas chromatography (capillary column, CPSIL5, 25 m), 250 or 400 MHz proton NMR and carbon-13 NMR spectroscopy. No (Z) was detected by these techniques. Dienes, described in this letter, were therefore considered more than 95% pure. However in another experiment, phenylacetaldehyde gave in the same conditions 1-phenyl-2,4-pentadiene. By gas chromatography coupled with mass spectrometry, two isomers (ratio 91/9) were detected; the major isomer was identified by proton and carbon-13 NMR as the (E) isomer.
5. 1,3-dibromopropene (b.p.$_{14}$= 53-58°C) prepared from 1-bromopropene (Aldrich) by standard bromination (see Fieser and Fieser, vol. 1, p. 191) was converted to 1-bromo-3-iodopropene (b.p.$_{13}$= 77-80°C; E/Z = 30/70) with NaI in acetone at reflux.
6. Gift of J.M. Vatèle; present address Harvard University, Cambridge (MA),USA.
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16. The trimethylsilylallyltri-n-butylstannane is a functionnalized allylstannane which was isolated and allowed to react with aldehydes in the presence of a Lewis acid to give either (E) or (Z) dienes; see Y. Yamamoto, Y. Saito and K. Maruyama, J.C.S.Chem.Comm. 1326 (1982).
17. In a parallel experiment, allyl bromide was allowed to react overnight at 70°C with $SnCl_2$ to yield CH_2=CH-CH_2SnCl_2Br, which was isolated[18] and identified by proton and carbon-13 NMR; this allylstannane was allowed to react (one hour at -20°C) with benzaldehyde in toluene to yield the homoallylic alcohol PhCH(OH)CH-CH=CH_2 in 54% yield.
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    T. Kauffmann, R. König, R. Kriegesmann and M. Wensing, Tetrahedron Lett., 25, 641 (1984).
20. Reaction of benzaldehyde with 1,3-dibromopropene and 2 equivalents of $SnCl_2$ gave (E) 1-phenyl-1,3-butadiene in 40% yield.
21. Reaction of allylstannanes with α,β-enones in the presence of a Lewis acid leads to opposite regioselectivity; see A. Hosomi, H. Iguchi, M. Endo and H. Sakurai, Chem.Lett., 977 (1979).

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