

A CONVENIENT SYNTHESIS OF FUNCTIONAL [2-<sup>2</sup>H]CYCLOHEXA-1,4-DIENES VIA  
VINYL ORGANOTIN REAGENTS

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**SUMMARY**

1- and 6-substituted [2-<sup>2</sup>H]cyclohexa-1,4-dienes were prepared by the electrophilic cleavage of tin-vinyl bonds in functional tributylstannyl-2-cyclohexa-1,4-dienes by deuteriated trifluoroacetic acid.

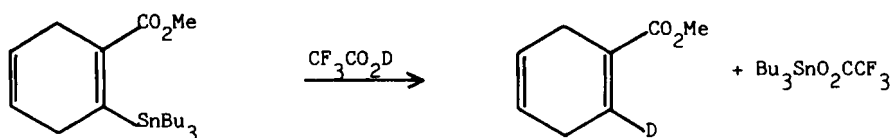
**KEY WORDS**

Deuterium labelling, vinyl organotins, functional[2-<sup>2</sup>H]cyclohexa-1,4-dienes, electrophilic cleavage.

Reactive tin-carbon bonds in organotins where the metal bears substituents as allyl, phenyl or vinyl groups are easily cleaved under mild conditions by halogens or acids (1). This property is of interest for the preparation of labelled compounds. Moreover, deuterium labelling via deuteriolysis of organotins gives generally higher isotopic purities than direct deuteriolysis of Grignard reagents or lithium derivatives (2). On the other hand, in some cases where these latter compounds are not available, organotins constitute an interesting alternative to reach the target labelled molecules.

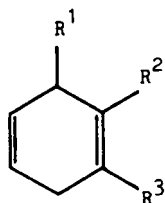
We reported recently the reversal of selectivity in SE<sub>2</sub> cleavage of mixed functionality tetraorganotin compounds by iodine (3). For instance, in 1-carbomethoxy-2-tributylstannylcyclohexa-1,4-diene (1), the tin-butyl bond

is cleaved preferentially to the more labile tin-vinyl bond. We then studied the protonolysis of (1) and did not observe the same inversion of reactivity: the tin vinyl bond was cleaved first, as expected from the literature (2) to give (2) where the tin atom was replaced by an hydrogen (4). By using deuteriated trifluoroacetic acid we obtained the same cleavage which gave a deuterium incorporation higher than 97%. This cleavage has been extended with success to the preparation of [2-<sup>2</sup>H]cyclohexa-1,4-dienes bearing acetyl, cyano or alkyl substituents (4)-(7) from the corresponding tin derivatives (8)-(11) as starting materials.



The preparation of 1-carbomethoxy[2-<sup>2</sup>H]cyclohexa-1,4-diene (3) has already been reported (5). It involved the low-yield cycloaddition (33%) of [3-<sup>2</sup>H]propionic acid and butadiene at 54°C, followed by an esterification. If a better yield was desired, the reaction had to be conducted at higher temperature which resulted in deuterium scrambling and low isotopic purity.

Our method is thus a very convenient way to the preparation of 2-labelled functional cyclohexa-1,4-dienes.



	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>
(1)	H	CO <sub>2</sub> Me	Bu <sub>3</sub> Sn
(2)	H	CO <sub>2</sub> Me	H
(3)	H	CO <sub>2</sub> Me	D
(4)	H	COMe	D
(5)	Me	CO <sub>2</sub> Me	D
(6)	H	CN	D
(7)	Me	COMe	D
(8)	H	COMe	Bu <sub>3</sub> Sn
(9)	Me	CO <sub>2</sub> Me	Bu <sub>3</sub> Sn
(10)	H	CN	Bu <sub>3</sub> Sn
(11)	Me	COMe	Bu <sub>3</sub> Sn

## EXPERIMENTAL

Preparation of compounds (1), (8), (9), (10), (11) by the high yield Diels-Alder reactions of methyltributylstannylpropionate, 1-tributylstannylbutyn-3-one or tributylstannylpropynenitrile with 1,3-butadiene or 1,3-pentadiene, has already been reported (6).

Deuteriolysis of the organotins : a typical procedure is the following. Trifluoroacetic acid-d (Aldrich)(8,7 mmol, 1g) was slowly added at room temperature to a solution of 7 mmol of organotin compound in 20 ml of dry pentane. The reaction mixture was stirred for 30 mn. The solvent was then evaporated under vacuum and the residue distilled in a Kugelrohr apparatus (oven temperature : 120°) at 30 mmHg. Yields : 90-94%. Deuterium incorporation, as measured by <sup>1</sup>HNMR and mass spectrometry, was found to be better than 97%.

<sup>1</sup>HNMR (CCl<sub>4</sub>) ( ppm/TMS)

<u>3</u>	2.87 (s, 4H) ; 3.70 (s, 3H) ; 5.80 (s, 2H)
<u>4</u>	2.30 (s, 3H) ; 2.85 (m, 4H) ; 5.65 (m, 2H)
<u>5</u>	1.05 (d, 3H) ; 2.6-3.2 (m, 3H) ; 3.80 (s, 3H) ; 5.5-5.9 (m, 2H)
<u>6</u>	2.80 (s, 4H) ; 5.70 (s, 2H)
<u>7</u>	0.95 (d, 3H) ; 2.15 (s, 3H) ; 2.6-3.2 (m, 3H) ; 5.3-5.8 (m, 2H).

## ACKNOWLEDGEMENTS

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