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Synthesis and Rearrangement of (Z)-Allylic Trichloroacetimidates.

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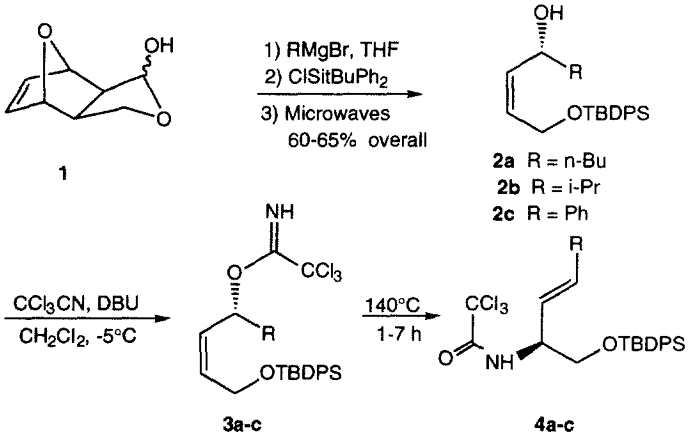
***Abstract** : An efficient synthesis of (Z)-allylic trichloroacetimidates starting from lactol 1 is described. Thermal [3,3] rearrangement of these imidates occurred with excellent chirality transfer to give allylic amides.* © 1999 Elsevier Science Ltd. All rights reserved.

***Keywords** : [3,3] rearrangements, allylic imidates, allylic amides, chirality transfer.*

The rearrangement of allylic imidates and in particular of allylic trichloroacetimidates, reported for the first time by Overman,[1] has been these last few years the subject of active investigations [2] since this transposition allows the synthesis of allylic amines which are useful synthons for the preparation of various nitrogen-containing compounds. This reaction is synthetically attractive because it is known to occur generally with excellent selectivity and chirality transfer. If numerous thermal or metal catalyzed rearrangements of (E)-allylic trichloroacetimidates to allylic trichloroacetamides have been reported in the literature, examples of rearrangement of (Z)-allylic imidates are relatively scarce. [2a,c,g] We report in this note a stereoselective and efficient synthesis of (E)-allylic amides via the thermal rearrangement of (Z)-allylic trichloroacetimidates easily prepared from the lactol **1** available in both enantiomeric forms from the corresponding lactones.[3]



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Treatment of the racemic lactol **1** with different Grignard reagents in tetrahydrofuran gave rise with high stereoselectivity (~ 90%), following a *like* approach, to the corresponding bicyclic diols. Protection of the primary hydroxy group, followed by retro Diels-Alder reaction using microwaves, led to the (Z)-monoprotected allylic diols **2a-c**. It must be noted that microwaves were particularly useful for these cycloreversions since quantitative yields were obtained in a few minutes (150°C, 30 min). A specific effect of microwaves was observed which greatly accelerated the reaction: under classical heating (150°C, oil bath) the conversion was only 15% after 30 minutes.[4] Reaction of alcohols **2** with trichloroacetonitrile in the presence of DBU gave the trichloroacetimidates **3a-c** which, without any purification [5] were rearranged to (E)-trichloroacetamides **4a-c** in refluxing xylenes (74-79% overall yields for the two steps).

The (E)-configuration of the double bond in **4** has been determined by the value of the coupling constants, measured in the ^{1}H NMR spectra, between the two ethylenic protons (J = 15.5 to 16 Hz).

Starting from enantiomerically enriched **2a** (ee = 94%), after formation of the imidate and thermal rearrangement, the allylic trichloroacetamide **4a** [6] was isolated with 93% of enantiomeric purity (determined by HPLC with a chiralcel OD-H column), showing that the thermal transposition occurred with a total transfer of chirality. In contrast with a recent report [7] concerning the rearrangement of (E)-allylic trichloroacetimidates, no rearrangement of the (Z)-compounds **3a-c** was observed when these compounds were exposed to catalysts such as mercury II or palladium II species.

In conclusion we described in this note a short (5 steps from **1**) and efficient (44 to 51% overall yield) synthesis of protected (E)-allylic amines, useful synthetic intermediates.

References and Notes

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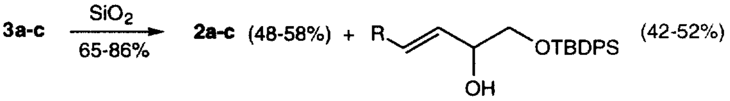
3. Bloch, R.; Guibé-Jampel, E.; Girard, C. *Tetrahedron Lett.* **1985**, *26*, 4086-4090.
4. Microwave irradiations have been made with the kind collaboration of Dr A. Loupy.
5. Attempts of purification by chromatography on silica gel led to two stereomeric alcohols with racemization :



6. We thank Dr M. Larchevêque for providing us with the spectral and physical data of **4a**.
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