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Preparation of Olefins from Alcohols by Thermal Rearrangement of Propargylic Xanthates

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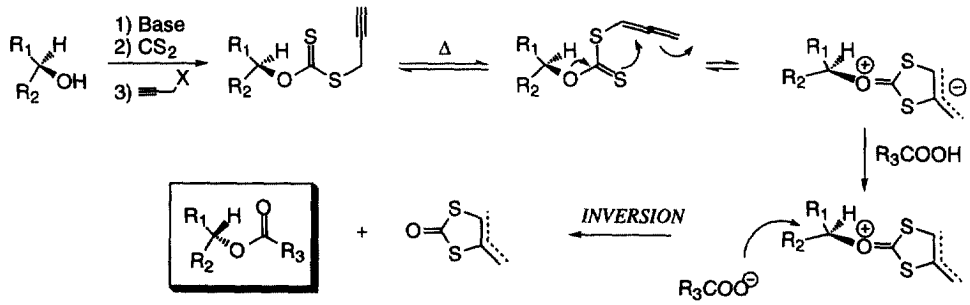
***Abstract** : Upon heating in toluene in the presence of a catalytic amount of collidinium trifluorosulfonate salt, various S-propargylic xanthates derived from secondary alcohols can be easily converted to their corresponding olefins in good yields.*

The large number of existing olefin-forming elimination reactions reflects the importance of alkenes as synthetic intermediates and as ultimate targets.[1] Because of this prominence, new reagents and processes are constantly being developed which offer some advantage over known procedures for alkene formation.[2]

Several methods are thus known for the dehydration of alcohols to olefins. Earlier approaches involved acid catalysed dehydration or base induced elimination of the corresponding halide, mesylate, or tosylate.[3] These somewhat harsh conditions do not always tolerate sensitive functionalities. Martin *et al.*[4] proposed a milder method of dehydration involving sulfuranes, and this was successfuly applied for example to the preparation of calciferols[5] and pyrethroid amides.[6] Burgess *et al.*[7] reported the preparation of methyl(carboxysulfamoyl)triethyl ammonium hydroxide inner salt and showed it to be a useful reagent for mild dehydration of primary alcohols. Crabbé,[8] Caspi[9] and many others interested in total synthesis[10] have demonstrated the applicability of this reaction to various polyfunctional molecules.

Other routes to alkenes include the pyrolysis of *p*-tolylthiocarbonates,[11] carbamates,[12] *N*-methyl-4-alkoxypyridinium iodides,[13] or xanthates (Chugaev reaction).[14] Yields are often reasonable, but carbon skeleton rearrangements can occur, due to the high temperature involved. Thermal decomposition of alkoxides of magnesium, zinc, and aluminium represents another alternative, but isomerisation remains a potential problem.[15] Finally, conversion of alcohols into aryl selenides or sulfides constitutes a convenient and efficient way to introduce olefins through *syn*-elimination of the corresponding selenoxides or sulfoxides.[16]



Scheme 1

We recently reported[17] a new process for the synthesis of esters and for the inversion of secondary alcohols, which occurs upon refluxing a toluene or chlorobenzene solution of an *S*-propargyl xanthate derived from the appropriate secondary alcohol in the presence of a carboxylic acid (Scheme 1). As some olefins

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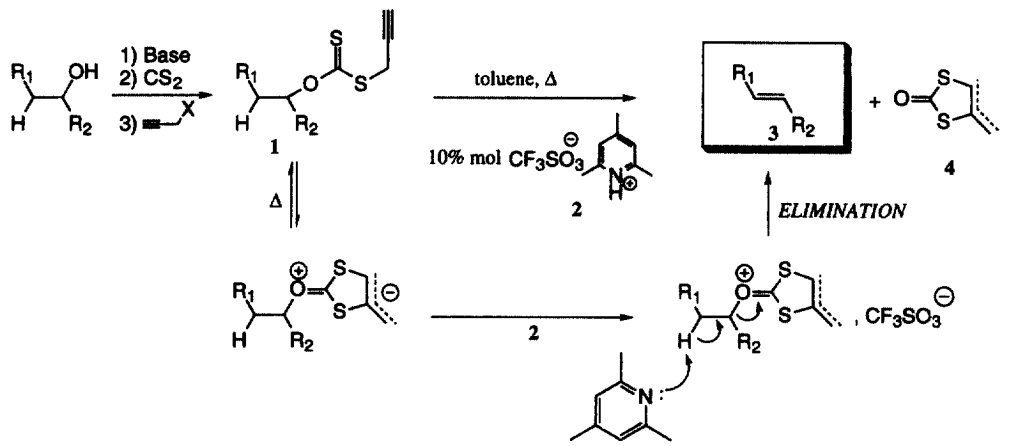
were isolated in some cases as by-products of the reaction, we modified the system to completely favour the olefins by refluxing the *S*-propargyl xanthates in toluene in the presence of a catalytic amount of collidinium trifluorosulfonate **2**. This salt, prepared by mixing collidine with an equivalent of trifluoromethanesulfonic acid in ether at 0°C, acts as a protonating agent for the betain, but is devoid of nucleophilic character.

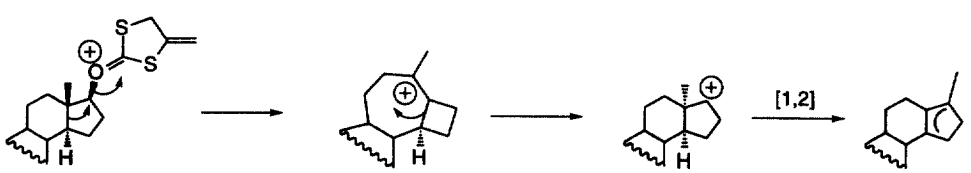
Our conception is outlined in Scheme 2. Salt **2** retains sufficient acidity to protonate the betain intermediate and convert it into a powerful leaving group. Collidine then mediates the β–elimination by removing the β–proton and regenerates salt **2** in the process. This leads to the formation of the desired olefin in good yield, as demonstrated by the examples collected in Table 1.



Scheme 2

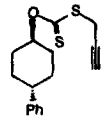
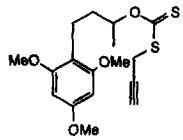
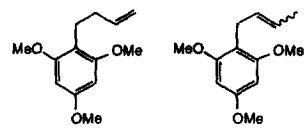
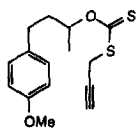
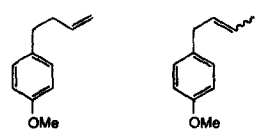
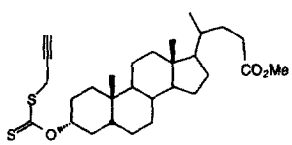
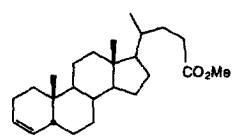
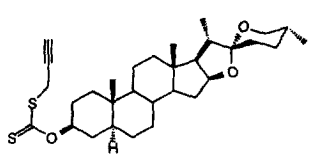
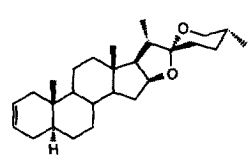
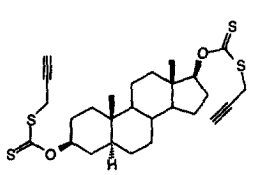
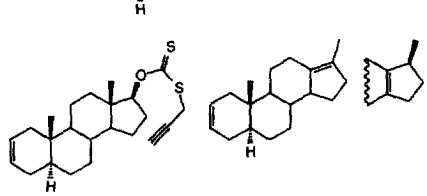
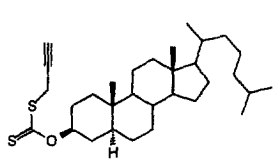
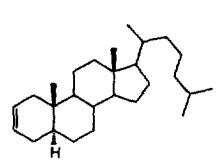
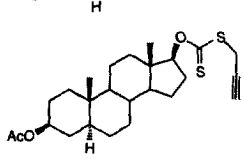
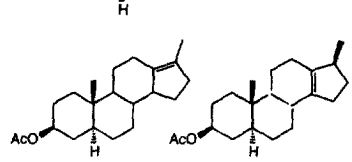
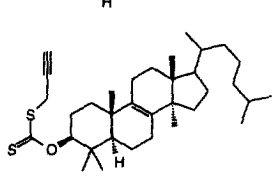
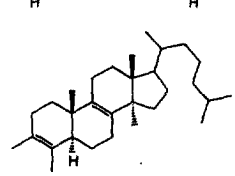
The simplicity of the method is worth underlining. The transformations described in this study were thus accomplished by mere heating *S*-propargylic xanthates **1** and the catalyst **2** (10 mol%) under reflux in toluene with stirring. The reactions were monitored by TLC and, after completion, the olefins **3**, uncontaminated with by-products other than the isomeric dithiolones **4**, were easily isolated by column chromatography.[18] For example, alkenes derived from steroidal alcohols are cleanly produced, as shown by the transformation of xanthate **1g** into olefin **3g** in 88% yield.

When the xanthate group is located at the 17-β position, as in **1f** and **1h**, direct elimination is slower than the cascade of Wagner-Merwein rearrangements which leads ultimately to a mixture of two isomers (**3f** and **3h** respectively), as depicted in Scheme 3. Because the 18-methyl carbon is not well positioned with respect to the leaving group, direct migration is stereoelectronically disfavoured in comparison with an initial ring D contraction. These results are consistent with the observations of Ohmori and co-workers.[19] .A similar — but this time direct— migration of a methyl group was observed in the case of terpene **1i**.



Scheme 3

Table 1 : Elimination reaction from *S*-propargyl xanthates

Entry	Xanthate (1)	Olefins (3)	Yields (%)
a			98
b			64 (20/80)*
c			75 (20/80)*
d			71
e			84
f			76** (50/50)*
g			88
h			quant. (50/50)*
i			61

* The isomers could not be separated; the proportions given were calculated from the ^{1}H NMR spectrum. For xanthates **1b** and **1c**, 4-aryl-2-butene were the major products.

** 14% of mono- and 62% of di-elimination products (the latter as a 1:1 mixture of isomers) were isolated after chromatography.

The thermal decomposition of *S*-propargyl xanthates in the presence of a mild non nucleophilic acid represents thus a facile means for the dehydration of secondary alcohols. Yields are good, although some isomerisation occurs in a few cases. Even relatively acid labile alcohols such as **1e** can be successfully dehydrated (extra amounts of pure collidine may be added to ensure a neutral medium in the case of especially sensitive substrates). It must be pointed out that no elimination occured when the propargylic xanthates were heated alone in toluene, indicating that the olefins were not formed through the classical Chugaev reaction, which in the case of secondary alcohols requires much higher temperatures.

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18. Typical experimental procedure : A solution of xanthate **1g** (0.5 mmol.) and salt **2** (0.05 mmol.) in toluene (5 ml) was heated to reflux for several hours. The solution was allowed to cool and the crude product was purified by chromatography after removal of the solvent to give 2-cholestene **3g** in 88% yield. Xanthates **1a**, **1b**, **1c**, **1d**, **1e**, **1f**, **1g**, **1h** and **1i** were obtained by alkylation with propargyl bromide of the xanthate salts derived from the respective alcohols and carbon disulfide.
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