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DEOXYGENATION OF ALLYLIC ALCOHOLS TO TERMINAL OLEFINS VIA STANNYLATION/DESTANNYLATION[1]

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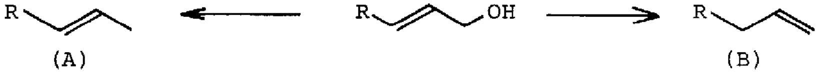
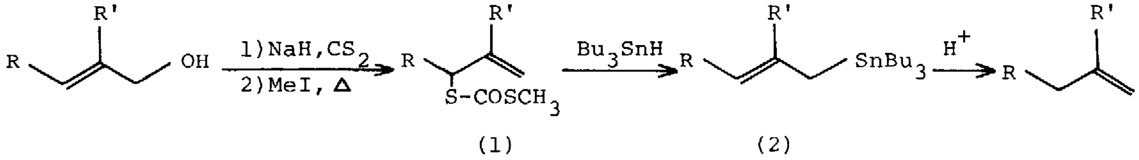
Summary; Deoxygenation of allylic alcohols to terminal olefins was performed via three steps; 1) [3,3]-sigmatropic rearrangement of O-allylxanthates, 2) the successive stannolysis with tributyltin hydride yielding allylic stannanes, and 3) final protolysis of allylic stannanes to terminal olefins.

In general, deoxygenation from oxygen-containing organic compounds is one of the most important transformations, since the many naturally occurring products are known to exsist both in oxygenated and their deoxygenated forms.

In fact, deoxygenation of allylic alcohols to methyl olefin (A) has been fully investigated by several workers.[2] On the other hand, no methodology which enables the effective deoxygenation to the energetically less stable terminal olefin (B) has been still established.

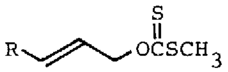


We wish to report here the new process based upon the strategy involving a stannylation and destannylation as outlined in Scheme 1.

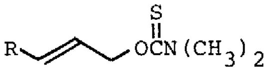


Scheme 1

The process inevitably requires the completely directed regiochemistry throughout the all reactions to avoid the contamination of the regioisomer. We have found the each transformation shown in Scheme 1 sufficiently satisfies our predefined criteria. First of all, we examined the allylic 1,3-functional group transposition (O→S) by use of [3,3]- or [2,3]-sigmatropic rearrangement of O-allylesters such as xanthate (3, in situ),[3] thionocarbamate (4),[4] diphenylphosphinothioate (5), or phenylsulfenate (6, in situ).[5]



(3)



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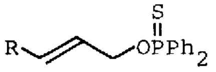


(5)

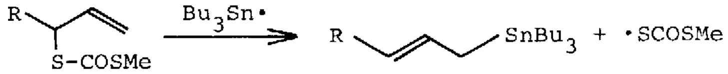
(6)

Among these O-allylesters, we found only O-allylxanthate (prepared in situ, from allylic alcohols by treatment with sodium hydride and carbon disulfide followed by methyl iodide) is practically useful for this purpose, giving the rearranged product, dithiocarbonates (1) in good yield under mild conditions (refluxing benzene for 2 hr)[6] (Table 1).

Allyl transfer from sulfur to tin (i.e. second step) was successfully visualized with tributyltin hydride involving S_H' process similar to more simple S-allyl sulfides or sulfones[8,9] (Table 1).

The general procedure is as follows. Dithiocarbonate (1) (1.8 mmol) and tributyltin hydride (3.6 mmol) in benzene (15 ml) containing catalytic amount of azobisisobutyronitrile (AIBN) were heated at 80°C for ca. 2 hr under N_2. After evaporation of benzene, the product was isolated by fractional distillation. It was found, however, that the employment of one equivalent of tributyltin hydride under the similar conditions gave better results (vide infra). The reaction scheme might be best explained by the following radical chain mechanism initiated by the attack of stannyl radical.

1

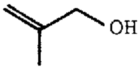
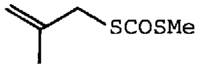
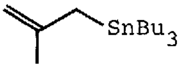
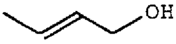
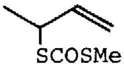
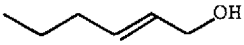
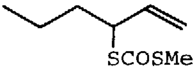
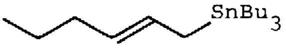
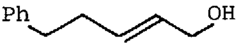
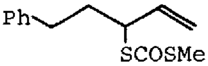
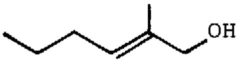
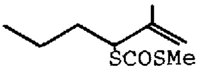
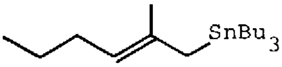
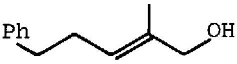
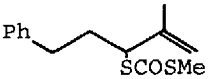
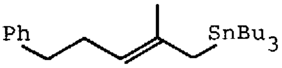
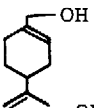
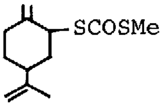
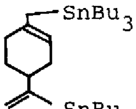
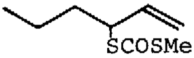


2 $\cdot SCOSMe \longrightarrow COS\uparrow + MeS\cdot$

3 $MeS\cdot + Bu_3SnH \longrightarrow MeSH\uparrow + Bu_3Sn\cdot$

4 $MeSH + Bu_3SnH \longrightarrow Bu_3Sn\text{-}SMe + H_2\uparrow$

Table 1. S-Allylic Dithiocarbonates and Their Stannylation[11]

Run	Allylic Alcohols	Dithiocarbonates (1)	Yield (%)	Allylic Stannanes[a)] (2)	bp[b)] (°C)	Yield (%)
1			79		110° (0.3mmHg)	78
2			64		120° (0.1mmHg)	84
3			86		120-125° (0.1mmHg)	73
4			87		175-183° (0.12mmHg)	86
5			62		160-165° (0.15mmHg)	77
6			70		120-123° (0.15mmHg)	59
7			89		170-178° (0.2mmHg)	86
8			74		140° (0.04mmHg)	91
9[c)]			56		150-155° (0.07mmHg)	80
10[c)]			86		125-130° (0.4mmHg)	82

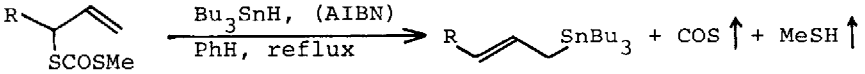
a) For convenience, only one stereoisomer is described in this report.

b) Kugelrohr distillation.

c) Equimolar amount of Bu_3SnH was employed.

When the twice molar amount of tributyltin hydride was employed, small amount of methylthiotributylstannane ($MeS-SnBu_3$) in addition to the trace amount of hexabutyldistannane ($Bu_3Sn-SnBu_3$), unreacted tributyltin hydride, and dibutyltin oxide (Bu_2SnO) was detected by GLC analysis.

More interestingly, as indicated in Run 9 and 10 (Table 1), employment of an equimolar amount of tributyltin hydride resulted in the formation of allylic stannane also in good yield with the formation of the negligible amount of the by-products described above. This fact indicates that the overall reaction under the equimolar conditions, giving only the desired allylic stannane, should be formulated as follows.[10]



All the gaseous by-products in this stannylation reaction clearly makes the present process practically more attractive for the preparation of allylic stannanes than our previously reported method starting from allylic sulfides or sulfones,[8,9] since the complete separation of allylic stannanes from sulfur-containing tin compounds such as phenylthiostannane ($PhS\text{-}SnBu_3$) or tolylsulfonylstannane ($TlSO_2SnBu_3$) is sometimes troublesome or difficult.

Facile protolysis of allylic stannanes to terminal olefins is well known process.[12] Consequently, the overall transformation provides the regiospecific deoxygenation of allylic alcohols to the terminal olefins as shown in Scheme 1.

References

1) Synthetic reactions using organotin and sulfur compounds. For part 3, see ref 9.

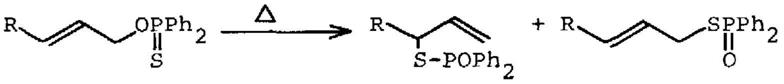
2) E. J. Corey and K. Achiwa, Tetrahedron Lett., 1837 (1969); J. Org. Chem., 34, 3667 (1969). F. Bohlmann, J. Staffeldt and W. Skuballa, Chem. Ber., 109, 1586 (1976).

3) K. Harano and T. Taguchi, Chem. Pharm. Bull. (Tokyo), 20, 2348, 2357 (1972).

4) R. E. Hackler and T. W. Balko, J. Org. Chem., 38, 2106 (1973).

5) D. A. Evans and G. C. Andrews, Acc. Chem. Res., 7, 147 (1974).

6) The [3,3]-sigmatropic rearrangement of the compounds (5) and (6) resulted in the formation of the mixtures of the regioisomers as shown below in the case of compound (5). While the rearrangement of (4) was very slow to get the appreciable amount of the rearranged product. See, ref 7.



7) T. Nakai and A. Ari-izumi, Tetrahedron Lett., 2335 (1976).

8) Y. Ueno and M. Okawara, J. Amer. Chem. Soc., 101, 1893 (1979).

9) Y. Ueno, S. Aoki and M. Okawara, ibid., 101, 5415 (1979).

10) In fact, the characteristic smell of mercaptan was observed during the reaction.

11) All new products obtained here had satisfactory spectral and physical data.

12) For the protolysis of allylic stannanes, see ref 9 and references cited therein.

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