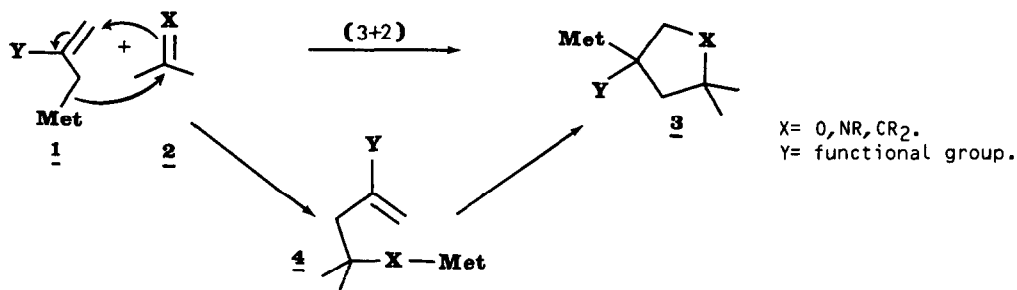


5-Endo-Trigonal ring closures of unsaturated sulfones.

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Summary :

The γ -functionalized unsaturated sulfones **5a-5d**, **8**, **11** and **15** respectively cyclize to the 5-membered heterocycles **6a-6d**, **9**, **14** and to the 5-membered carbocycle **16** in good yields. These ring closures are all 5-Endo-Trig processes.



Scheme_1

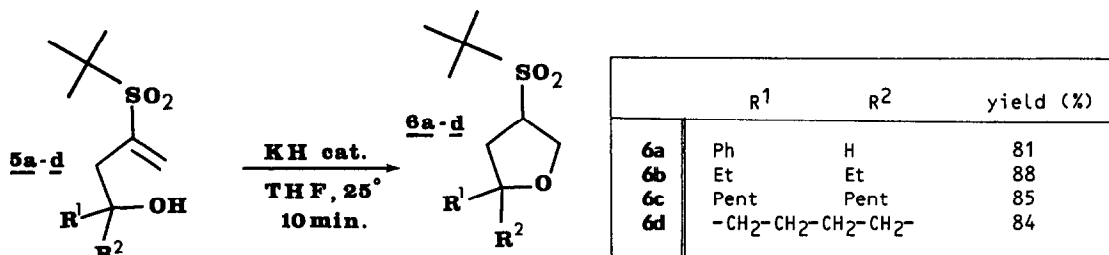
(3+2) cycloadditions between an allylic organometallic compound of type **1** bearing an electron-withdrawing group at position 2 and an unsaturated molecule of type **2** (leading to a functionalized 5-membered heterocyclic or carbocyclic organometallic compound of type **3**) are potentially useful in organic syntheses <1> (see scheme 1).

Some recent studies showed us that the desired cycloaddition did not always occur, instead the hydrolysis products derived from **4** were isolated in good yields <2> (see scheme 1). Thus, in the case where the cycloaddition of compounds **1** and **2** is a two step reaction, the second step (e. g. the ring closure of **4** to **3**) is a disfavored 5-Endo-Trig ring closure <3> which is not a common reaction <3, 4>.

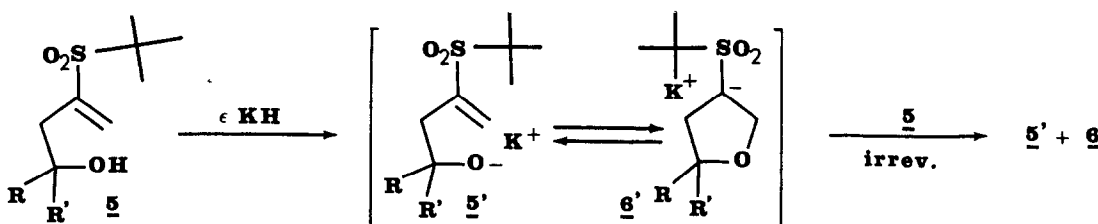
We find now that a proper choice of the metal Met, of the functional group Y, and of the reaction conditions allows cyclization of **4** to compounds of type **3** in high yields <5> : thus treatment of the easily available <2c> vinyl-sulfones **5a-d** with a catalytic amount of potassium hydride (5%) in THF for 10 min. at 25° affords the 3-tert-butylsulfonyl-tetrahydrofurans **6a-d** in 81-85% yield (see the table).

The following mechanism is proposed : deprotonation of the sulfone **5** with potassium hydride furnishes the corresponding potassium alcoholate which is in equilibrium with the cyclic carbanion **6*** (see scheme 2). This carbanion abstracts irreversibly the hydroxy proton of **5** leading to the tetrahydrofuran **6** and to the potassium alcoholate **5'** which starts the catalytic cycle again. The equilibrium between the cyclic and open-chain anions **5'** and **6*** is proven as follows : treatment of the tetrahydrofuran **6c** with 2.5 equivalents of n-butyllithium in THF (1hr. , -78°) leads to the sulfone **7** in 78 % yield (see scheme 3). In this case, the addition of n-butyllithium to the unsaturated sulfone shifts the equilibrium to the open-chain form, whereas protonation of the cyclic form **6*** shifts the equilibrium to the ring closed compound **6**.

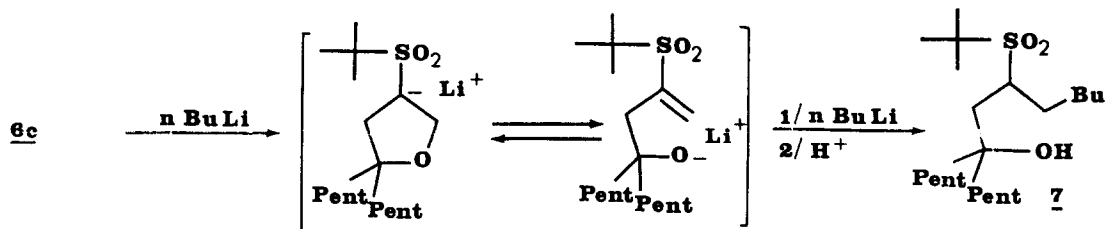
Table

Ring closure of the hydroxy-sulfones **5a-d** to the tetrahydrofurans **6a-d**.

The given yields are those of flash chromatographically purified material. All spectroscopic data (IR. , ¹H-NMR and ¹³C-NMR) are compatible with the shown structure.

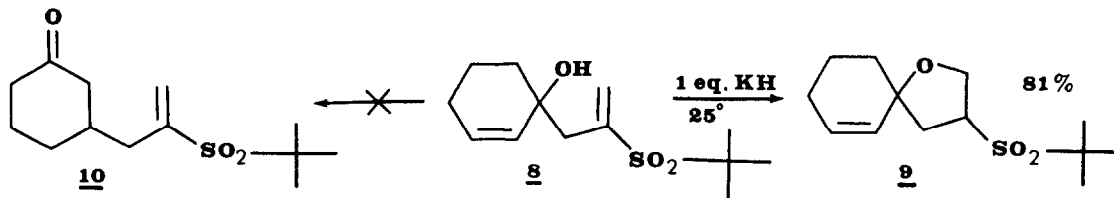


Scheme_2



Scheme_3

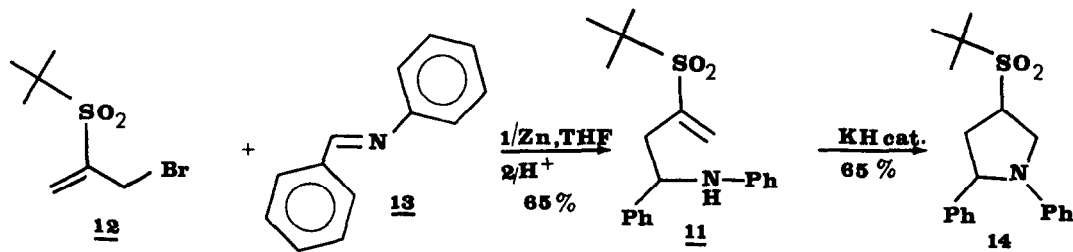
Under our conditions these 5-Endo-Trig ring closures are fast reactions; thus when the hydroxy-sulfone **8** (<2c> is treated with one equivalent of potassium hydride in THF, we observed the formation of the 5-Endo-Trig cyclization product **9** and not of the product **10** which would result from the usually fast Oxy-Cope reaction (<6> (see scheme 4).



Scheme_4

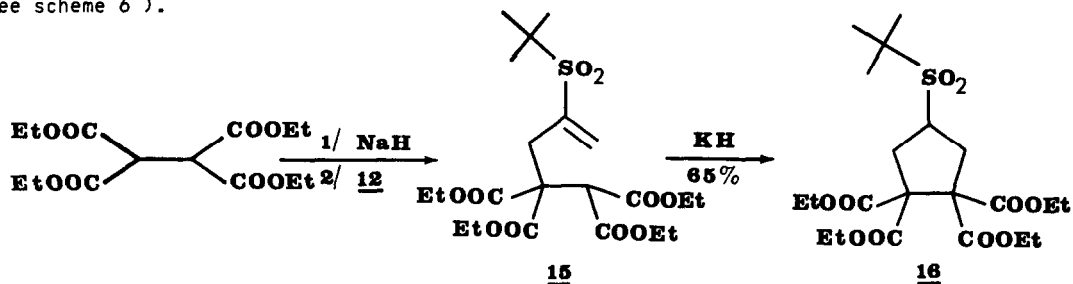
The presence of the sulfonyl group in compounds **5** is essential for the ring closure; thus the sulfoxide corresponding to **5a** (SO instead of SO₂) (<7> gives no cyclic product when treated with potassium hydride and only decomposition occurs.

The γ-amino-sulfone **11** obtained by addition of the 3-bromo-2-(tert-butylsulfonyl)-1-propene **12** (<2c> to the imine **13** in the presence of zinc (45°, 0.5 Hr. , 65%) gives a similar ring closure when treated with a catalytic amount of potassium hydride leading to the pyrrolidine **14** in 65 % yield (see scheme 5).



Scheme 5

In the same way the tetraester **15** obtained from the commercial tetraethyl-1, 1, 2, 2-ethanetetracarboxylate and the sulfone **12** (1 eq. NaH, THF, 25°, 0. 5 Hr. , 95% yield) furnishes the functionalized 5-membered ring **16** in 65 % yield (5% mol eq. of KH, 0. 5 hr. , 45°; see scheme 6).



Scheme 6

Thus under the proper conditions and with the suitable substrates, 5-Endo-Trig cyclizations are feasible reactions and allow us to realise a formal (3+2) cycloaddition of the compounds of type **1** and **2** to obtain the 5-membered rings of type **3** (X = O, NR, CR₂ ; see scheme 1).

Extension of these 5-Endo-Trigonal ring closing processes to other compounds of type **4** are presently under study.

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of cis and trans 3-nitro-2-phenyl-tetrahydrofurans in 30.5 % yield ; we thank professor J.
E. Baldwin for sending us these results prior to publication
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- <7> This compound is obtained by treatment of 3-bromo-2-(tert-butylsulfinyl)-1-propene with
benzaldehyde in 95 % yield. The preparation and reactivity of 3-bromo-2-(tert-
-butylsulfinyl)-1-propene will be reported later.

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