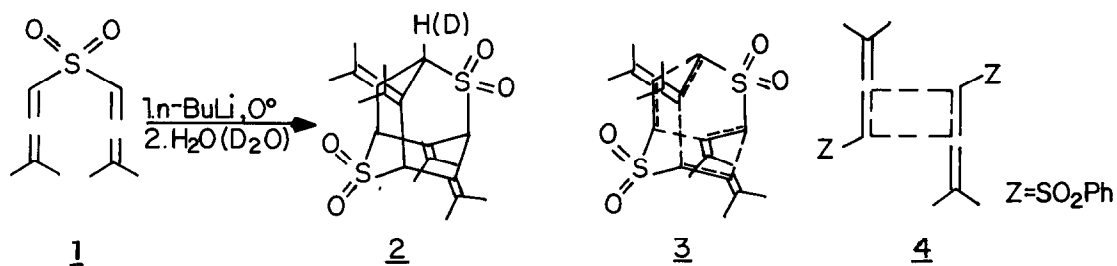


SYNTHETIC APPLICATIONS OF THE CARBANION WALK MECHANISM: A NOVEL AND
FACILE METHOD FOR THE PREPARATION OF 1,3-DIMETHYLENECYCLOBUTANE AND
CONJUGATED VINYLALLENE DERIVATIVES.¹

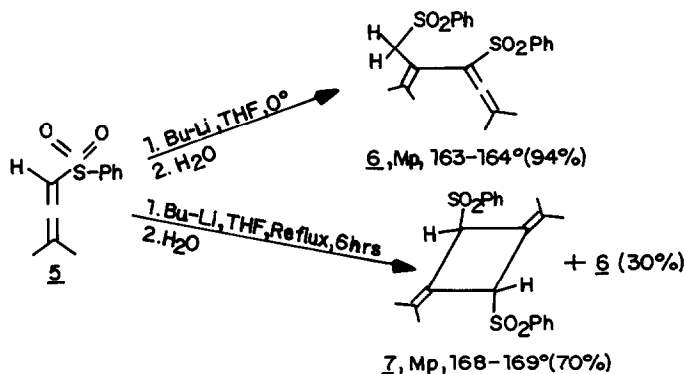
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Summary: Treatment of allenyl sulfone 5 with one half equivalent of n-BuLi in refluxing THF affords a mixture of two dimers: 1,3-dimethylenecyclobutane 7 and vinylallene 6. At 0°C, only the second product is obtained. In contrast, treatment of the same sulfone (5) with a full equivalent of n-BuLi, followed by addition of α,γ,γ -trimethylallenyl phenyl sulfone results in the exclusive formation of 1,3-dimethylenecyclobutane 14, even at low temperatures.

One of the most interesting and best studied reactions of allenes², both mechanistically and stereochemically, and one of the most useful reactions synthetically, is their thermal cyclodimerization to dimethylenecyclobutanes.^{2a-c,3} However, of special interest appears to be the long standing observation that while allene itself undergoes dimerization at high temperature to a mixture of 1,2- and 1,3-dimethylenecyclobutane in a ratio of 85:15, respectively^{2a,4}, none of the later type of dimerization has been reported as being formed in the case of substituted allenes.^{2,3} Consequently, and in view of the theoretical, spectroscopic^{5a-c} and chemical^{5d} interest in 1,3-dimethylenecyclobutane derivatives in the past, several tedious multistep synthetic schemes for their preparation had to be used.⁶

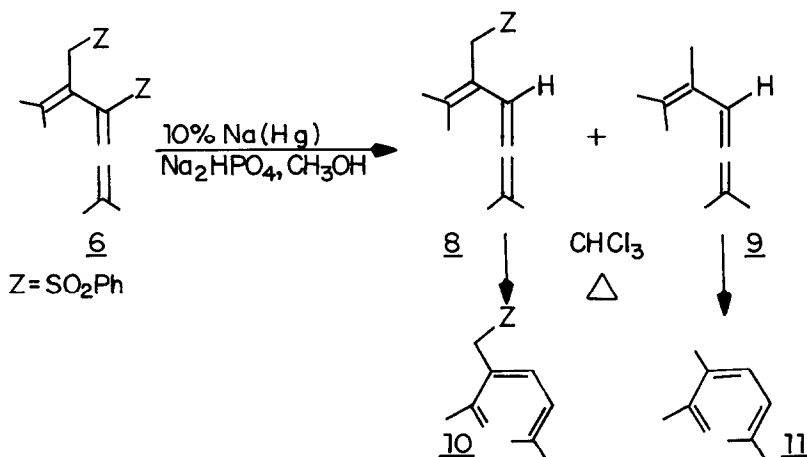


Previously, we have reported an unexpected base catalyzed cyclodimerization of bis- γ,γ -dimethylallenyl sulfone (1) to the 2,6-dithiaadamantane derivative 2, and explained its formation by a "carbanion walk mechanism", in which an allenic α -sulfonyl carbanion initiates a series of four consecutive inter-intramolecular Michael additions with final return of the negative charge to its original carbon atom, as illustrated by a dashed line in 3.⁷ Prompted by these results, and in order to test the generality of this mechanism, we have decided to investigate the predictable base catalyzed cyclodimerization of mono-allenic sulfones to 1,3-dimethylenecyclobutanes (see 4).

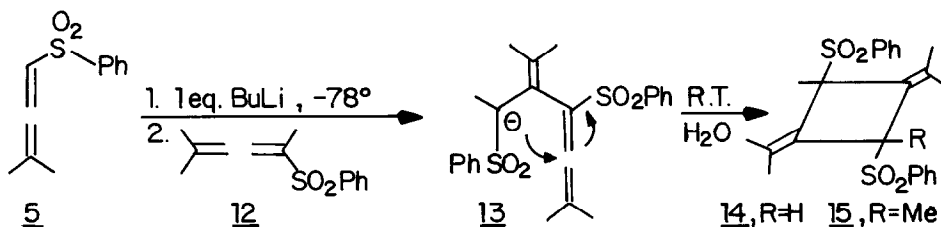


Treatment of a solution of γ,γ -dimethylallenyl phenyl sulfone (5)⁸ in THF with one half equivalent of *n*-butyllithium at 0°C, resulted in dimerization of the substrate and formation of the conjugated vinylallene derivative 6,⁹ as the only product. However, if the same reaction is carried out at reflux temperature for six hours, the expected cyclo-dimer 7⁹ is obtained, together with the open isomer 6, thus indicating a temperature dependent equilibrium between the two isomers. Obviously, formation of a 1,3-dimethylenecyclobutane requires a higher activation energy than formation of the 2,6-dithiaadamantane skeleton.¹⁰ Besides their mechanistic significance, both reactions are of considerable synthetic utility, especially after reductive desulfurization. For example, vinylallenes¹¹ have been of particular interest recently due to their facile thermal [1,5]-sigmatropic hydrogen shift to conjugated hexatrienes of well defined configuration.¹²

Reduction of vinylallene 6 with excess 10% Na-Hg in methanol at room temperature for several hours¹³ gave a 1:1 mixture of the monodesulfonylated product 8 and completely desulfonylated product 9, indicating easier allenic than allylic desulfonylation. Reflux of the two vinylallenes 8 and 9 in chloroform for twelve hours, after chromatographic separation, resulted in their quantitative isomerization to the substituted (*Z*)-1,3,5-heptatrienes 10 and 11, respectively. The generality of the base catalyzed dimerization of the allenyl sulfone 5 to vinylallene 6 has been demonstrated by the dimerization of γ -methyl- γ -ethylallenyl and γ -methyl- γ -phenylallenyl sulfones to the corresponding vinylallenes,



under the same conditions. Surprisingly, on attempted preparation of a "mixed" vinylallene, by the procedure described below, we have observed a different type of behaviour.



Reaction of γ,γ -dimethylallenyl phenyl sulfone (**5**) with *n*-butyllithium in a 1:1 ratio at -78°C gave the corresponding allenyl anion which, on addition of one mole of γ,γ,γ -trimethylallenyl phenyl sulfone (**12**)¹⁴ at the same temperature, followed by heating to room temperature and quenching with water, resulted in the formation of the 1,3-dimethylenecyclobutane derivative **14**,⁹ as the only product. Although the spectral evidence was in accord with the assigned structure of **14**, unequivocal structure proof was obtained by X-ray crystallographic analysis (Figure 1), which also indicates a trans configuration for the two sulfonyl groups. If quenching of the reaction was done with iodomethane, instead of water, the symmetrical 1,3-dimethylenecyclobutane **15** was the only product observed⁹, as indicated by two singlets in a 2:1 ratio for all the methyl groups, in its ¹H NMR spectrum. Exclusive cyclization to the expected 1,3-dimethylenecyclobutane has also been observed on treatment of the carbanions derived from γ -methyl- γ -ethylallenyl and γ -methyl- γ -phenylallenyl phenyl sulfones with allenyl sulfone **12**, under the same conditions.

The contrast observed between the exclusive formation of the 1,3-dimethylenecyclobutane **14** on one hand and the exclusive formation of the vinylallene **6** on the other hand, can be explained in terms of the general mechanism suggested for the formation of both products. Apparently, the ease of cyclization to compound **14** or **7** is controlled by the relative stability of the allylic carbanion in the corresponding vinylallene precursors to a considerable extent. The reduced stability of the allylic anion **13** as a result of electronic destabilization by the additional α methyl group, as well as decreased allylic resonance stabilization

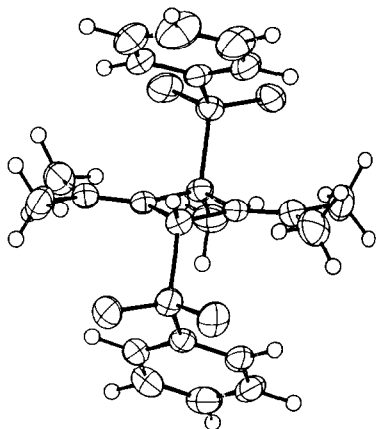


Figure 1. An ORTEP drawing of the molecular structure of 14 as determined by X-ray analysis. Crystal data: Monoclinic, $P2_1/c$, $a = 8.831(5)$, $b = 12.907(2)$, $c = 19.789(4)$ Å, $\beta = 92.05(3)^\circ$, $z = 4$. The structure was solved by direct and Fourier methods and refined anisotropically (nonhydrogen atoms only) by least-squares using 2000 reflections with $I > 3\sigma(I)$. The final discrepancy index is $R = 0.046$

as a result of steric crowding between the two α and γ methyl groups, seem to favour a shift in the equilibrium to the cyclic carbanion of 14, which enjoys double allylic stabilization and disappearance of mentioned steric effects. Finally, since allenic sulfones are readily obtained by [2,3]sigmatropic rearrangement of propargylic sulfinates⁸, the above reactions are a very convenient approach to the title compounds.

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