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A NOVEL CARBANIONIC CYCLODIMERIZATION OF DIALLENYL SULFONES TO 2,6-DITHIAADAMANTANE DERIVATIVES[1]

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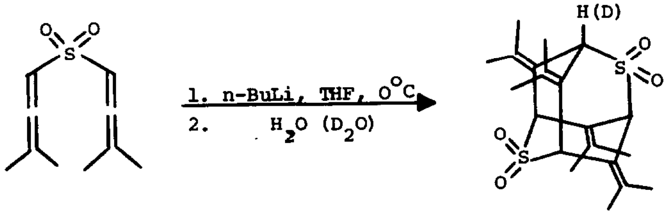
The thermal cyclodimerization of allenes to 1,2-dimethylenecyclobutanes has been of long-standing interest because of its synthetic utility and of its mechanistic aspects. Consequently, a vast amount of work has been performed on monoallenes[2]. In contrast, the study of diallenic systems has received relatively little attention in the past[3]. Recently, we have reported that bis-γ,γ-dimethylallenyl sulfone (1) undergoes a facile and quantitative thermal cyclization to 3-isopropenyl-4-isopropylthiophene-1,1-dioxide[3a] and a spontaneous electrophilic fragmentation-cyclization to α,β-unsaturated γ-sultines[3e].

In continuation, we have also studied the behaviour of the diallenyl sulfone 1 under basic conditions. Surprisingly, we have found that treatment of a solution of 1 in tetrahydrofuran or ether with n-butyllithium at 0° results in a novel and fast dimerization-cyclization of the diallenyl sulfone to give the 2,6-dithiaadamantane derivative 2, mp, 260° (d); ^{1}H nmr ($CDCl_3$, 100 MHz): δ 1.97 (s,24H), 5.20 (s,4H); ^{13}C nmr ($CDCl_3$, 20 MHz): δ 21.68 (Me), 61.20 ($CHSO_2$), 119.38 & 137.10 (C=C); ir ($CHCl_3$), 1100 (s), 1300 (s), 1645 (w) cm^{-1}; ms: M^+ absent, m/e 332 (M^+-SO_2), 268 (100%), 225; Calcd. for $C_{20}H_{28}S_2O_4$: C, 60.6; H, 7.1; S, 16.2. Found: C, 60.4; H, 7.0; S, 16.2; (yield 60%).



1 2

Although the spectral evidence was in accord with the assigned structure of 2, unequivocal structure proof was obtained by X-ray crystallographic analysis (Figure 1).

The cyclodimerization of 1 is of considerable interest on several accounts. Since diallenic sulfones can be obtained conveniently by a double [2,3]-sigmatropic rearrangement of propargylic sulfoxylates[3a], the conversion of 1 to 2, represents a facile synthesis of a dithiaadamantane system. The extension of this reaction to other bridged diallenic

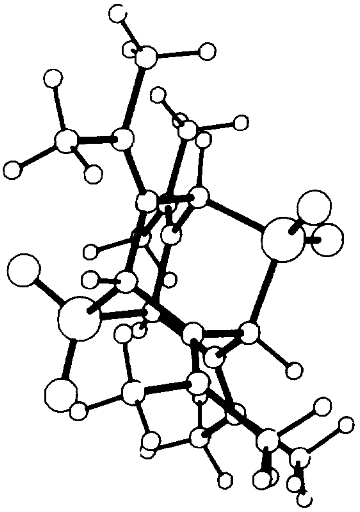
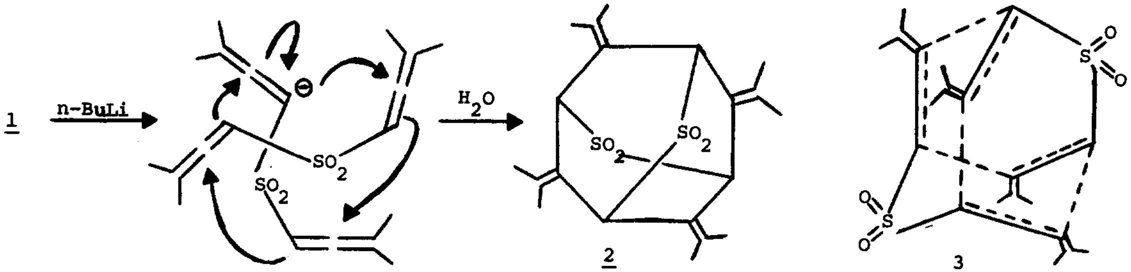


Figure 1. A structural view of 2 as determined by X-ray analysis. Crystal data: Monoclinic, $P2_1/c$, $a = 14.130$, $b = 9.327$, $c = 16.366$ Å, $\beta = 106.35^\circ$, $Z = 4$. A data set of 4781 reflections was measured on a CAD3 diffractometer using Mo-K_α radiation. The structure was solved by direct methods and refined anisotropically by least squares using 2984 observed reflections (3σ). Final discrepancy indices are $R = 0.076$, $R_w = 0.062$. Averaged bond distances: S-O 1.432(2), S-C 1.792(3), C=C 1.329(12), C-C 1.513(11) Å. Full details will be published elsewhere.

systems is currently under investigation in our laboratory. To the best of our knowledge, this appears to be the first reported example of a base-catalyzed cyclodimerization of an allenic system. The dimerization of 1 may be explained by a novel mechanism (Scheme I) in which an allenic α-sulfonyl carbanion initiates a process named by us "carbanion walk" or "carbanion tour" the path of which is illustrated by a dashed line in 3, with no claim for concertedness.

Scheme I



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