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TOWARDS A MOLECULAR-SIZE CONSTRUCTION SET: $3,3^{(n-1)}$-BISACETYLTHIO[n]STAFFANES

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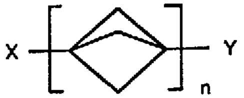
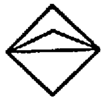
Abstract: Synthesis and properties of a series of staffanes **1[n]**, n = 1-5, functionalized with an -SR group at both termini are reported.

It has been proposed recently[1-3] that [n]staffanes **1[n]** (X = Y = H), oligomers of [1.1.1]propellane[4] **2**, represent nearly ideal building blocks for a molecular-size civil engineering set for the construction of various objects of Nanotechnology.[5] The preparation of [n]staffanes with a single terminal substituent (X ≠ H, Y = H) by oligomerizing radical addition of 2 across X-H bonds, and the introduction of a second terminal substituent Y = COCl by subsequent chlorocarbonylation, have already been described.[2]

In order to obtain doubly functionalized telomers in a single step, we have examined the radical addition of 2 across the S-S, P-P, Si-Si, Sn-Sn, C-S, C-Hal, S-Hal, Si-Hal, P-Hal, Sn-Hal, Se-Hal, and Hal-Hal bonds of several dozen reagents. Only a few yielded the desired oligomers. The reagent of choice is diacetyldisulfide (X = Y = $SCOCH_3$), which afforded the first five oligomers (**1[n]**, n = 1-5).



1[n]



2

UV irradiation of **2**[6,7] and $(CH_3COS)_2$ in diethylether followed by distillation, crystallization, and gradient sublimation yielded analytically pure $3,3^{(n-1)}$-bisacetylthio[n]staffanes (**1[n]**, X = Y = $SCOCH_3$, n = 1-5) in individual yields ranging from ~20% to less than 1%. They are thermally stable up to ~280°C; the trimer and higher oligomers form liquid crystals.[8] X-ray structure determination (Figure 1) on two crystal modifications of 1[3] (X = Y $SCOCH_3$) showed that the "syn" (dihedral angle, 14°) and "anti"

(144° in one modification, 177° in the other) conformers have very similar structures, characterized by remarkably short interbridgehead C-C bonds (1.46-1.47 Å). The presence of short bonds was predicted[9] and has also been found in [2]staffanes.[1-3,10] It is readily understood from hybridization arguments. The [n]staffane length increment from n to n+1 is 3.35 Å.

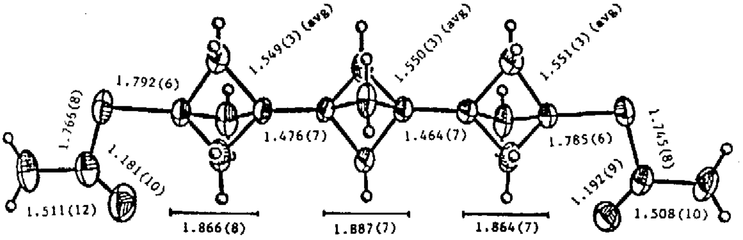


Figure 1. X-ray structure of the "syn" conformer of 3,3"-bisacetylthio[3]staffane

The ^{1}H and ^{13}C NMR chemical shifts follow a simple pattern (Figure 2) which can be described by use of additive increments.[3]

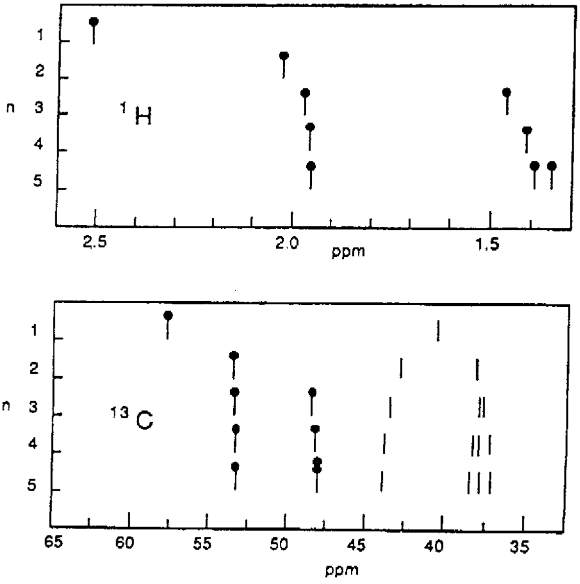
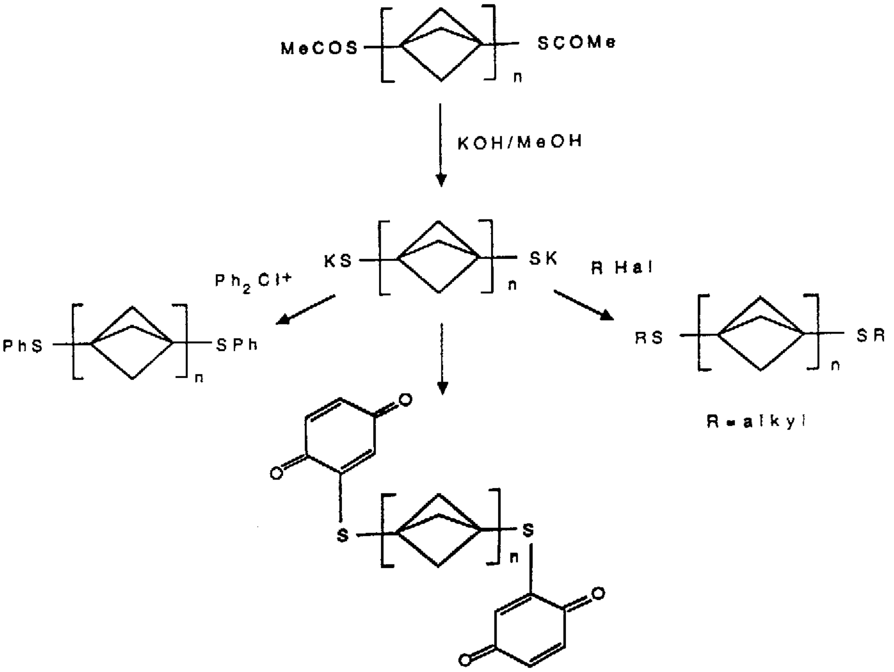
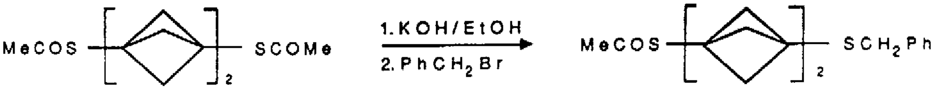


Figure 2. ^{1}H and ^{13}C NMR shifts in $3,3^{(n-1)}$-bisacetylthio[n]staffanes (1[n], X = Y = $SCOCH_3$)

The bisacetylthio[n]staffanes are readily hydrolyzed to dithiolates, and these can be transformed further with trivial ease:



The termini have also been differentiated by partial hydrolysis and subsequent substitution:



This synthetic versatility of the bisacetylthio[n]staffanes is important for their intended use in a molecular "Tinkertoy"[11] construction set.

We find that dipivaloyldisulfide does not add to 2 under these conditions, nor does di-*t*-butyldisulfide, but simpler dialkyldisulfides and diaryldisulfides do, although they do not always yield oligomers. In a private communication, Prof. Szeimies (Munich) has informed us that several dialkyl and diaryldisulfides were added to 2 in his laboratory, and several resulting oligomers up to n = 3 were isolated.[10]

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11. Tinkertoy is a trademark of Playskool, Inc., and designates a children's toy construction set consisting of straight beams and connectors.

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