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A FACILE AND UNEXPECTED SYNTHESIS OF TWO NOVEL CONDENSED HETEROCYCLES: 1,1,4,4-TETRAMETHYL-1H,4H-THIENO[3,4-*c*]THIOPHENE AND 1,1,4,4-TETRAMETHYL-1H,4H-SELENOLO[3,4-*c*]SELENOPHENE

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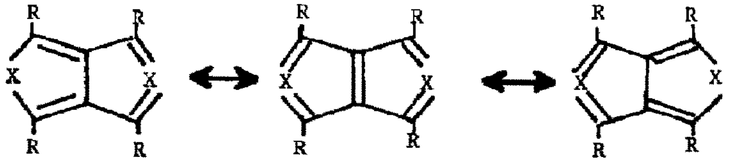
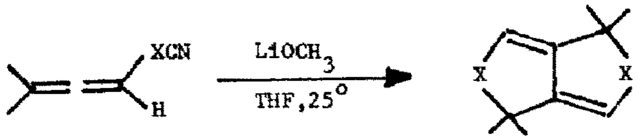
Summary: The title compounds, 5 and 7, have been synthesized by the action of lithium methoxide on γ,γ-dimethylallenyl thiocyanate and selenocyanate, respectively. A multi-step mechanism involving bis-γ,γ-dimethylallenyl disulfide or diselenide, as key intermediates, is suggested.

Of the various possible isomeric thienothiophenes,[1] the nonclassical thieno[3,4-*c*] thiophene 1[2] has been of most general interest, since the uncharged resonance contributors of this 10π-electron system are structures containing tetracovalent sulfur. Although the parent molecule 1 has so far escaped isolation, its tetraphenyl derivative 2 is remarkably stable, and has been synthesized by an elegant approach by Cava and coworkers,[3] who have also studied, among others, its electronic structure.[4,5] Recently, the synthesis of tetraphenylselenolo[3,4-*c*]selenophene (3) has been reported, by Gronowitz and coworkers.[6] The syntheses of these compounds involved their corresponding 1,3-dihydroderivatives, as key intermediates. The parent 1H,3H-thieno[3,4-*c*]thiophene and several of its derivatives have been previously reported by Zwanenburg and Wynberg.[7] However, to the best of our knowledge, there are no previous literature reports of any corresponding 1,4-dihydro derivatives. We now wish to report a surprising one-step synthesis of 1,1,4,4-tetramethyl-1H,4H-thieno[3,4-*c*]thiophene (5) and its diselenium analogue (7).



1 X = S, R = H
2 X = S, R = ϕ
3 X = Se, R = ϕ

4 X = S
6 X = Se



5 X = S
7 X = Se

The starting material for the synthesis of 5 was γ,γ-dimethylallenyl thiocyanate (4),[8] which is conveniently prepared by an S_N2' displacement reaction by thiocyanate anion on α,α-dimethylpropargyl bromide.[9] Treatment of compound 4 with lithium methoxide in THF at room temperature for eight hours under nitrogen, gave compound 5, as a crystalline solid,

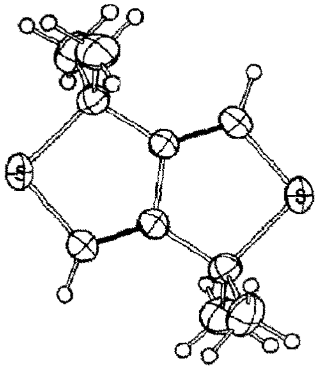


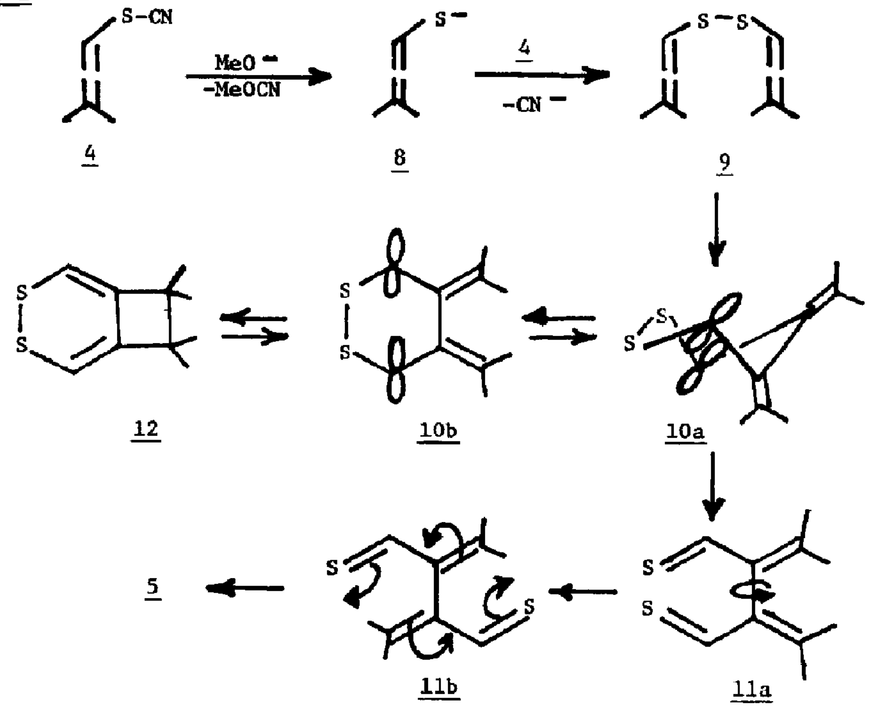
Figure 1. An ORTEP drawing of the molecular structure of 5 as determined by single-crystal X-ray analysis. Crystal data: Monoclinic, $P2_1/c$, a = 8.517(2), b = 6.109(1), c = 10.730(1) Å, β = 107.01(2)°, Z = 2. The structure was solved by direct methods and refined anisotropically (50% probability thermal ellipsoids are shown) by least-squares using 1059 reflections with $I \geq 4\sigma(I)$. The final discrepancy index is R = 3.2%. Bond distances are: $C(sp^3)$-$C(sp^3)$ 1.524 and 1.529, $C(sp^3)$-$C(sp^2)$ 1.508, $C(sp^2)$-$C(sp^2)$ 1.440, $C(sp^2)$=$C(sp^2)$ 1.338, $C(sp^2)$-S 1.749 and $C(sp^3)$-S 1.867 Å; the C-S-C bond angle is 93.4°. Full details will be published elsewhere; the atomic parameters are deposited at the Cambridge Crystallographic Data Center.

mp, 134°(d); ^{1}H nmr ($CDCl_3$,60 MHz) δ 1.56 (s,12H), 5.76 (s,2H); ^{13}C nmr ($CDCl_3$, 20 MHz): δ 31.30 (Me), 53.64 (C1&4) 114.68 & 151.11 (C=C); ir ($CHCl_3$), 1650 (m) cm^{-1} ; uv (EtOH): λ_{max} (ϵ_{max}) 270 (12,000), 330 (13,000): ms: m/e 198 (M^+, 48%), 183 (100%); Calcd. for $C_{10}H_{14}S_2$: C, 60.60; H, 7.07; S, 32.32. Found: C, 60.56; H, 7.09; S. 32.45 (yield 70%).

Unequivocal structure proof of 5 was also obtained by X-ray crystallographic analysis (Fig. 1), in order to exclude the cyclobutano-1,2-dithiin 12, which is mechanistically a conceivable product (*vide infra*). The synthesis of compound 7[8] is analogous to that of 5, except for the use of γ,γ-dimethylallenyl selenocyanate (6)[8], as starting material.

Both compounds 5 and 7 are believed to be formed by the same multistep mechanism as illustrated in Scheme 1, for the formation of 5. The supporting evidence for this mechanism is as follows. Although undetected in the course of the reaction, the formation of *bis*-γ,γ-dimethylallenyl disulfide (9) by reaction of 4 with methoxide ion is quite reasonable in view of the results obtained with ethyl thiocyanate, which gives diethyl disulfide under the same conditions, as well as on account of literature reports on the transformation of alkyl and aryl thiocyanates into disulfides by treatment with alkaline reagents.[10] While we are unaware of previous reports on bisallenyl disulfides, they are undoubtedly excellent candidates for the thio-Cope rearrangement, due to the very low energy of the sulfur-sulfur bond in α,β-unsaturated disulfides,[11a] and the relatively easy thermolysis of disulfides in general.[11b] Further support is provided by the facile thermal [3,3]-sigmatropic rearrangement of the structurally related divinyl disulfides which in certain cases is spontaneous even at low temperatures.[12] Consequently, the rearrangement of the bisallenyl disulfide 9 to the conjugated dienic dithial intermediate 11a, by either a concerted [3,3]sigmatropic rearrangement,[13] or by a diradical mechanism[14] appears plausible. The latter mechanism has been the one preferred for the analogous thermal gas phase rearrangement of various ethano bridged bisallenes, including the parent 1,2,6,7-octatetraene.[14] While the gas phase thermolysis of this compound at 310°C gave only 3,4-dimethylene-

Scheme 1



1,5-hexadiene,[14d] the reaction at 120° gave also bicyclo[4.2.0]octa-1,5-diene.[14b] The latter compound is believed to be formed through a planar 2,3-dimethylene-1,4-cyclohexadiyl diradical.[14a-c] The absence of 12 in the present work, may therefore be the result of one or more of the following reasons. It may either reflect the lack or poor conversion of the twisted bisallyl diradical 10a, in its chair conformation, into the planar diradical 10b, due to the fast ring opening of 10a to give 11a, or, alternatively, it may reflect the considerable steric and ring strain expected for structure 12. Conversely, and in view of the published work on the ethano bridged bisallenes,[14] as well as on the low thermal stability of 1,2-dithiins,[15] it is not impossible that 12, although formed, undergoes spontaneous ring opening to 11a, the same intermediate as obtained directly from 10a (Scheme 1). On the basis of the well known instability of thioaldehydes in general, and their tendency to undergo spontaneous dimerization or polymerization,[16] our failure to isolate, or even detect, the dienic dithial 11, is hardly surprising. Finally, rotation around the central C-C σ bond of 11a, by 180 degrees brings the molecule into the requisite conformation (11b) for the operation of a double intramolecular Michael-type addition to give the observed reaction product 5, as indicated by the arrows in 11b, with no claim for concertedness. As stated earlier, the mechanism presented in Scheme 1, is also suggested for the transformation of 6 into 7. It is worthwhile noting, that this transformation is also easily and quantitatively achieved by the heating of a solution of 6 in 50% aqueous hypophosphorous acid at 60° for 2 hours. Based on the recent report by Cava and coworkers[17] on the formation of dibenzyl ditelluride from benzyl tellurocyanate, as well as formation of dibenzyl diselenide[8] from benzyl selenocyanate, in our hands, under the same conditions, this result provides further support to the intermediacy of bis-γ,γ-dimethylallenyl diselenide.

Further mechanistic and stereochemical aspects of the reactions described above as well as the chemistry of the two new condensed heterocycles, are under investigation.

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