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REARRANGEMENTS OF BRIDGED DIALLENES. A FACILE SYNTHESIS OF NOVEL CONDENSED HETEROCYCLES BY TANDEM [3,3]-SIGMATROPIC REARRANGEMENT AND DOUBLE INTRAMOLECULAR MICHAEL ADDITION OF DIALLENYL DISULFIDES AND DISELENIDES. ISOLATION OF STABLE DIALLENYL DISELENIDES.[1]

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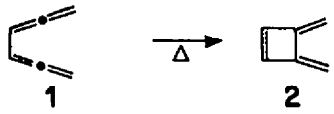
Abstract - Thienothiophene **14** and selenoloselenophene **16** have been synthesized by the action of lithium methoxide on τ,τ-dimethylallenyl thiocyanate and selenocyanate, respectively. A multistep mechanism involving *bis*-τ,τ-dimethylallenyl disulfide (**20**) or diselenide as key intermediates, is suggested. The latter are believed to undergo consecutive [3,3]-sigmatropic rearrangement and double Michael addition, to the observed products. This mechanism is supported by the isolation of *bis*-τ,τ-diisopropylallenyl and *bis*-τ-methyl-τ-isopropylallenyl diselenides, under the same reaction conditions, and the rearrangement of the latter to the expected selenoloseleophene **33**. The synthesis of the novel mixed selenolothiophene **35** by treatment of a mixture of allenyl thiocyanate **13** and selenocyanate **15** with lithium methoxide, is also described.

INTRODUCTION

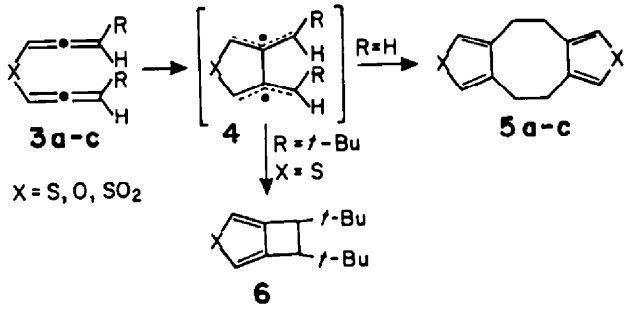
Although the chemistry of monoallenes[2] has been studied extensively since the first authentic synthesis of propadiene, over a hundred years ago,[3] the chemistry of diallenes has received considerable attention only during the last two and a half decades.[4] One of the best studied and most useful reactions of allenes in general, and of diallenes in particular, are molecular rearrangements. However, since this subject has been extensively reviewed, also very recently.[5] only a brief summary of its major features is presented below.

As expected, some of the first studied rearrangements of diallenes involved conjugated diallenes. Similar to conjugated dienes, these compounds undergo thermal electrocyclization to derivatives of 3,4-dimethylenecyclobutenes (Eq. 1),[6] and have been suggested as intermediates in the rearrangement of 1,5-hexadiynes to the same type of products.[7] However, it has been recently shown[6d] that the position of the electrocyclic equilibrium between **1** and **2** is in distinct contrast to that of the electrocyclic equilibrium between butadiene and cyclobutene, in which the former is heavily favored enthalpically.



1 2 (1)

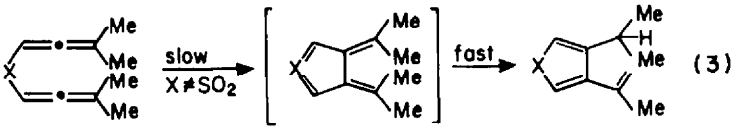
Rearrangements are not limited to conjugated diallenes, but have also been observed with appropriately bridged systems, such as, π, heteroatom and ethano bridged diallenes as well.[5] With this type of compounds, rearrangements are strongly dependent on the nature of the bridge and allenyl substitution. For example, with unsubstituted π and heteroatom bridged allenes **3a–d**, obtained by carefully controlled base catalyzed isomerization of the corresponding 4-heterohepta-1,6-diynes at 0° or below, dimerization at room temperature or above to the respective dimers **5a–d** (R=H) has been suggested to proceed by a bisallylic biradical intermediate **4**.[6] Such biradicals, also known as tetramethyleneethanes, have often been discussed as reactive intermediates in thermal dimerization of allenes.[7] On the other hand, with τ-monosubstituted diallenes, such as *bis*-τ-*t*-butylallenyl sulfide (**3a**, R=*t*-butyl), a formal 2+2 cycloaddition to the cyclobutanothiophene derivative **6** took place by the same type of mechanism.[8]



3a-c **4** **5a-c** (2)

6

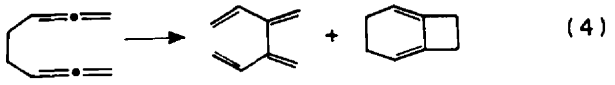
In contrast to the above example, we have previously shown that *bis*-τ,τ-dimethylallenyl systems undergo a remarkably facile cyclization by a formal intramolecular ene reaction, in practically quantitative yield.[10,11] However, while the cyclization of *bis*-τ,τ-dimethylallenyl sulfone (**7a**) to the thiophene-1,1-dioxide derivative **9a** has been suggested to take place by a 2,2'-bisallyl-type diradical mechanism, the cycloaromatization of bisallenes **7b–7d** to the corresponding products **9b–d** is believed to proceed by a two step mechanism.[10] involving formation of the quinodimethane intermediate **8b–d** in the first rate-determining step, followed by a fast-[1.5]hydrogen shift in the second step.



7a-d **8b-d** **9a-d**

(a) X=SO_2 (b) X=S (c) X=Se (d) X=C_6H_4

In addition to the rearrangements mentioned above, the Cope-type rearrangement of both cyclic[6a,12] and acyclic[6a,13] ethano bridged diallenes has also received considerable attention in the past. For example, the [3,3]-sigmatropic rearrangement of 1,2,6,7-cyclodecatetraene to 2,3-divinyl-1,3-cyclohexadiene at 300° has been reported by Skattebul[6a] and by Harris.[12] Somewhat analogous behavior has been reported for the thermal rearrangement of 1,2,6,7-octatetraene to 3,4-dimethylene-1,5-hexadiene and bicyclo[4,2,0]octa-1,5-diene (Eq. 4).[6a,13] The mechanism of the latter reaction is further discussed below.



10 **11** **12**

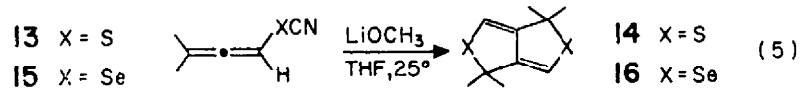
In view of our previous experience with the rearrangement of various π and monoheteroatom bridged diallenes, we decided to investigate the rearrangement of diheteroatom bridged diallenes, such as diallenyl disulfides and diselenides, which appeared to us as suitable candidates for rearrangement by at least one of the reaction patterns described above, and which, surprisingly, have escaped attention so far. We now report a detailed study of the synthesis and rearrangement of such systems which has resulted in the unexpected one-step synthesis of some novel condensed heterocycles, as well as apparently unprecedented isolation of certain stable diallenyl diselenides.[14]

RESULTS AND DISCUSSION

One of the reasons responsible for the lack of documentation on diallenic disulfides and diselenides, if not the major one, may well be the difficulties involved in their preparation. Indeed, one of the most useful syntheses of disulfides in general is the oxidation of the corresponding thiols.[15] However, since no information on allenic thiols seems to exist, we decided to examine an indirect method, which is relatively little known but quite promising due to ready access to starting materials, namely the reaction of organic thiocyanates with bases.[16] Previously, we have found[17] that unlike primary and secondary propargyl bromides which react with thiocyanate anion by simple S_N2 displacement, tertiary propargyl bromides react by an S_N2' mechanism, instead.

In view of our previous favorable experience with *bis*-τ,τ-dimethylallenyl systems,[10,11] we initiated our study with the preparation of *bis*-τ,τ-dimethylallenyl disulfide and diselenide. Consequently, τ,τ-dimethylallenyl thiocyanate (13), conveniently prepared by reaction of potassium thiocyanate with α,α-dimethylpropargyl bromide, was treated with freshly prepared lithium methoxide in THF at room temperature for eight hours under nitrogen. Surprisingly, instead of the expected *bis*-τ,τ-dimethylallenyl disulfide, a white crystalline and highly symmetrical molecule was obtained (70% yield), as indicated by two ^{1}H NMR singlets at δ 1.56 and 5.76 in the ration of 6:1. Assuming that the expected diallenyl disulfide was unstable and underwent spontaneous rearrangement and/or cyclization, the monocyclic 1,2-dithiin analogue of 9, resulting by a formal intramolecular ene reaction could also be ruled out by its ^{1}H NMR, but not the symmetrical cyclobutano-1,2-dithiin 23, which might have resulted from a formal intramolecular [2+2]cycloaddition. However, although both the ^{1}H and ^{13}C NMR spectral data were consistent with this structure, the UV absorption, λ_{max} 330 (ε =13,000), was not, since dithiins in general absorb in the visible and are red colored.[18]

Furthermore, unlike dithiins, which are readily converted to the corresponding thiophens on heating or UV irradiation, our product remained unchanged after two days of UV irradiation or heating at 130°. Similarly, no reaction was observed on attempted nucleophilic cleavage of the S-S bond using lithium thiophenolate in refluxing tetrahydrofuran for 20 hours,[19a] monodesulfurization using *tris*-dialkylaminophosphine in refluxing benzene for 12 hours,[19b] or reduction with LAH,[19c] as expected from a cyclic disulfide compound, even under much milder conditions.

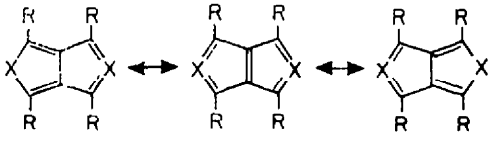


(5)

In view of the above, the structure of the product has been unequivocally determined as 1,1,4,4-tetramethyl-1H,4H-thieno-[3,4-c]thiophene (14) by X-ray crystallographic analysis, as previously reported.[14] Although this structure was not predicted, it is mechanistically a conceivable one (*vide infra*). The synthesis of 1,1,4,4-tetramethyl-1H,4H-selenolo[3,4-*c*]selenophene (16) is analogous to that of 14, except for the use of τ,τ-dimethylallenyl selenocyanate (15), as starting material.

Of the various possible isomeric thienothiophenes,[20] the nonclassical thieno[3,4-*c*]thiophene 17[21] has been of most general interest, since the uncharged resonance contributors of this 10 π-electron system are structures containing tetracovalent sulfur. Although the parent molecule 17

has so far escaped isolation, its tetraphenyl derivative **18** is remarkably stable, and has been synthesized by an elegant approach by Cava and coworkers,[22] who have also studied, with others, its electronic structure.[23] Subsequently, the synthesis of tetraphenylselenolo[3,4-*c*]selenophene (**19**) has been reported by Gronowitz and coworkers.[24] The synthesis 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.[25] However, to the best of our knowledge, there are no previous literature reports of any corresponding 1,4-dihydro derivatives.

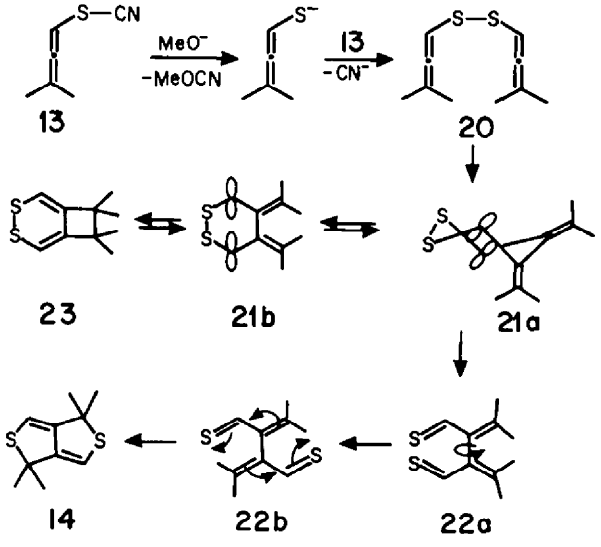


17 X = S, R = H
18 X = S, R = ϕ
19 X = Se, R = ϕ

Both compounds **14** and **16** are believed to be formed by the same multistep mechanism as illustrated in Scheme 1, for the formation of **14**. The supporting evidence for this mechanism is as follows. Although undetected in the course of the reaction, the formation of *bis*-τ,τ-dimethylallenyl disulfide (**20**) by reaction of **13** with methoxide ion is quite reasonable in view of the results obtained with ethyl thiocyante 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.[16] While we are unaware of previous reports on bisallenyl disulfides, they are undoubtedly excellent candidates for the dithio-Cope rearrangement due to the relatively low energy of the sulfur-sulfur bond in α, -unsaturated disulfides[26a] and the relatively easy thermolysis of disulfides in general.[26b] 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.[27] Consequently, the rearrangement of the bisallyl disulfide **20** to the conjugated dienic dithial intermediate **21a**, by either a concerted [3,3]-sigmatropic rearrangement,[28] or by a diradical mechanism[13] 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.[13] While the gas phase thermolysis of this compound at 310° gave only 3.4-dimethylene-1,5-hexadiene, the reaction at 120° gave also bicyclo[4.2.0]octa-1.5-diene.[13a] The latter compound is believed to be formed through a planar 2.3-dimethylene-1,4-cyclohexadiyl diradical.[13a,c] The absence of **23** 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 **21a**, in its chair conformation, into the planar diradical **21b**, due to the fast ring opening of **21a** to give **22a**, or, alternatively, it may reflect the considerable steric and ring strain expected for structure **23**. Conversely, and in view of the published work on the ethano bridged diallenes,[13] as well as the low thermal stability of 1,2-dithiins,[16] it is not impossible that **23**, although formed, undergoes spontaneous ring opening to **22a**, the same intermediate as obtained directly from **21a** (Scheme 1). On the basis of the well known instability of thioaldehydes in general, and their tendency to undergo spontaneous dimerization or polymerization,[27] our failure to isolate, or even detect, the dienic dithial **22** is hardly surprising. Finally, rotation around the central C-C σ bond of **22a** by 180° brings the molecule into the requisite conformation (**22b**) for the operation of a double intramolecular Michael-type addition to give the observed reaction product **14**, as indicated by the arrows in **22b**, with no claim to concertedness. As stated earlier, the mechanism presented in Scheme 1, is also suggested for the transformation of **15** into **16**. It is worthwhile noting, that this transformation is also easily and almost quantitatively achieved by the heating of a solution of **15** in 50% aqueous hypophosphorous acid at 60° for 2 hours. Based on the report by Cava and coworkers[30] on the formation of dibenzyl ditelluride from benzyl tellurocyanate, as well as formation of dibenzyl diselenide from benzyl selenocyanate in our hands under the same conditions, this

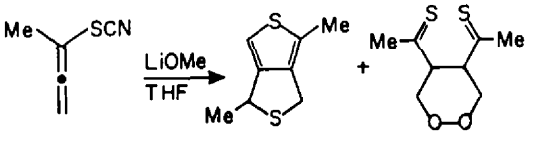
Scheme 1



result provides further support to the intermediacy of *bis*-τ,τ-dimethylallenyl diselenide.

However, in order to further prove the validity of the mechanism presented in Scheme 1, we have sought more direct evidence, such as the isolation or at least trapping of one or more of the proposed reaction intermediates. First, we attempted to trap the dienic dithial **22** with either SO_2 or tetracyano-ethylene, but without success. Next, we assumed that the stability of **22** might be substantially increased by conversion from a dithial to a dithioketone, which may be stable enough[31] to be isolated or at least detected spectroscopically. Consequently, the synthesis of α-alkyl or aryl substituted allenyl thiocyanates has been attempted, using several different approaches. The simplest approach appeared to be deprotonation of the available τ,τ-dimethylallenyl thiocyanate with base followed by alkylation of the α-allenyl carbanion. However, treatment of **13** with BuLi resulted in nucleophilic attack on sulfur, and formation of the corresponding sulfide, exclusively. This reaction was employed by us for the preparation of various allenyl ethynyl sulfides by reaction of **13** with the appropriate alkynyllithium reagent.[32] Similarly, the use of lithium diisopropylamide instead of BuLi, resulted in the formation of the same product as the one formed with LiOMe, described above. The second approach was to react trisubstituted propargyl halides such as α,α-dimethyl-τ-phenylpropargyl bromide with NaSCN. However, since this latter could not be prepared by the normal reaction of the alcohol with PBr_3, the corresponding chloride[33] was used instead. Interestingly, treatment of this compound with sodium thiocyanate in refluxing acetonitrile for one hour, resulted in elimination of HCl and formation of 3-methyl-1-phenylbutenyne in 82% yield. At room temperature, no reaction was visible even after 20 hours.

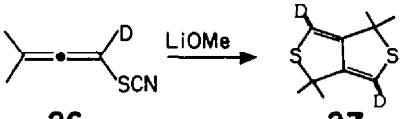
The last approach to prepare α-substituted allenyl thiocyanates was by base catalyzed isomerization of the corresponding α-substituted propargyl thiocyanates, but again without conclusive results. For example, treatment of α-methylpropargyl thiocyanate with lithium methoxide at room temperature afforded a complex mixture of product, together with a low yield of the expected product, and a 10% yield of a product which might be tentatively assigned a structure resulting from O_2 trapping of the dienic



24 **25** **26** (6)

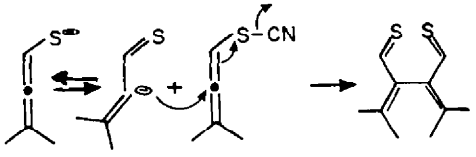
dithioketone intermediate (eq. 6).[34,35a,f,h] Formation of α-methylallenyl thiocyanate (24) in this reaction, was demonstrated by performing the reaction at -78° for one hour and isolation of a mixture of starting material and its tautomer (24). The behavior of this thiocyanate is similar to the unsubstituted one. Thus, treatment of propargyl thiocyanate with $LiOCH_3$ at room temperature results in immediate darkening and polymerization. The latter appears to be very fast even at -78°, although the propargyl-allene isomerization can be easily detected by NMR in this case as well.[34] The lack of stability of τ-unsubstituted allenyl thiocyanates is not surprising, in view of literature reports[35f,35e] that unsubstituted allenyl ethynyl or propargyl sulfides are also highly sensitive and decompose at room temperature exothermally.

The facile base catalyzed propargyl-allene thiocyanate isomerization described above has prompted us to investigate the stability of the τ,τ-dimethylallenyl thiocyanate under the reaction conditions. For this purpose, α-deuterio-τ,τ-dimethylallenyl thiocyanate (26), prepared according to the procedure described for the undeuterated compound (13), was subjected to the same reaction conditions. Formation of 1,1,4,4-tetramethyl-3,6-dideuterio-thieno[3,4-c]thiophene (27), as expected indicates the absence of any interaction of 13 with base, other than that shown in Scheme 1.



26 27

Isolation of Stable Diallenyl Diselenides. In view of the above results, which failed to provide conclusive evidence with regard to the intermediacy of the postulated dienic dithial intermediate (22), we attempted to obtain direct evidence for the intermediacy of the diallenyl disulfide or diselenide, especially in view of the possibility of formation of 22 by an alternative mechanism not involving such intermediates. As shown in Eq. 7, the dienic dithial intermediate could also result directly from the allenyl thiolate anion, if the latter attacked the thiocyanate substrate 13 by an S_N2'-type attack on the central allenic carbon by its valence isomer, rather than by the route shown in Scheme 1.



(7)

The use of Dreiding models of *bis*-τ,τ-dimethylallenyl disulfide (**20**) shows clearly that formation of the bond between the central allenic carbons requires that the molecule adopts a conformation in which the two sulfur atoms and two α-allenic carbons are coplanar, while two allenyl groups lie below and above that plane and are perpendicular to each other (Fig. 1). No interaction between the two allenyl groups is likely when they are parallel to each other, due to excessive steric hindrance between the τ-methyl groups. Even in the conformation shown in Fig. 1 the steric hindrance is already considerable and may represent a borderline case. Consequently, we reasoned that the use of bulky substituents at the τ-positions may well prevent the diallenyl disulfide or diselenide from further reaction, at least to the point of enabling its isolation. This prediction has been entirely borne our by experiment, as shown below.

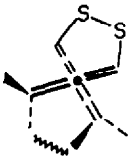
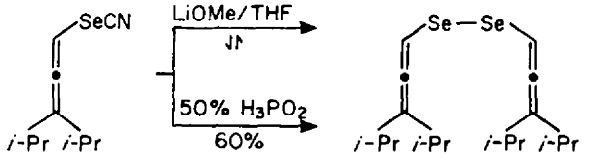


Fig. 1

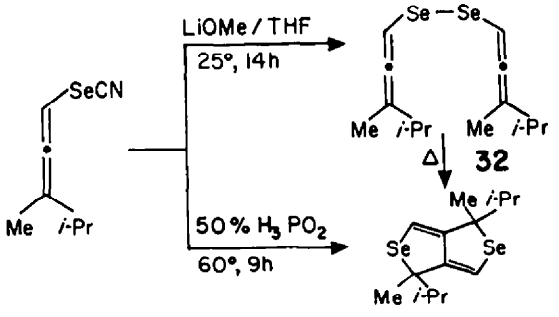
For this purpose, we first attempted the preparation of *bis*-τ,τ-diisopropylallenyl disulfide. α,α-Diisopropylpropargyl alcohol has been prepared by reaction of monolithium acetylide with di-isopropyl ketone. Although the corresponding bromide could not be prepared by the normal procedure, the chloride was readily obtained. However, to our disappointment, no reaction was observed between this chloride and sodium thiocyanate even on prolonged heating at high temperature, apparently due to decrease in reactivity of chloride, as leaving group. In sharp contrast, and to our delight, we found that the selenocyanate anion, a better nucleophile, reacts as usually and affords τ,τ-diisopropylallenyl selenocyanate (**28**) in good yield. Furthermore, treatment of the latter with either LiOMe in refluxing THF for 3 hours or with 50% aqueous H_3PO_2 at 60° for 2 hours, afforded the corresponding diselenide **29** in high yield. To the best of our knowledge, this appears to be the first isolable and stable diallenyl diselenide reported, and in accord with our prediction this compound was completely stable and remained unchanged even in



28 **29** (8)

refluxing acetonitrile or toluene, except for some decomposition during extended heating. In order to show that the lack of rearrangement of **29** is indeed due to steric effects, we have converted this compound into the corresponding monoselenide by the use of *tris*-diethylaminophosphine in refluxing benzene for 3 hours. Unlike *bis*-τ,τ-dimethylallenyl selenide (**7c**) which undergoes quantitative cyclization to the selenophene derivative **8c** at room temperature, *bis*-τ,τ-diisopropylallenyl selenide (**30**) remains unchanged even after two days of heating and refluxing acetonitrile.

So far, we have seen two extreme modes of behavior of allenyl selenocyanates with either lithium methoxide or H_3PO_2. At one extreme, using τ,τ-dimethylallenyl selenocyanate (**15**), one can isolate the final selenoselenophene only, while at the other extreme, using selenocyanate **28**, only intermediate diselenide **29** is isolated. Logically, one may predict that the use of some intermediate substitution such as τ-methyl-τ-isopropylallenyl selenocyanate, one may expect to observe both the corresponding diallenyl diselenide, as well as its rearrangement product. This expectation was also fully realized. Treatment of τ-isopropyl-τ-methylallenyl selenocyanate (**31**) with 50% aqueous H_3PO_2 at 60° for 9 hours afforded the rearrangement-cyclization product 1,4-dimethyl-1,4-diisopropylselenolo[3,4-c]selenophene (**32**) directly. On the other hand, treatment of **31** with LiOMe at room temperature overnight gave *bis*-τ-isopropyl-τ-methylallenyl diselenide (**32**). Furthermore, heating of the latter in refluxing acetonitrile solution for one hour afforded the condensed selenophene **33**, as expected.

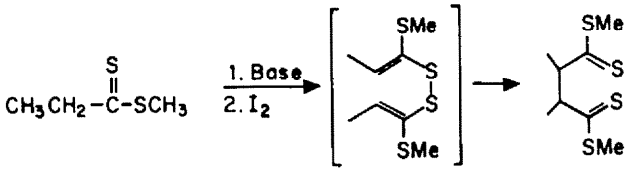


(9)

31 **33**

We believe that the results of the last experiment provide convincing evidence that the remarkable conversion of allenyl selenocyanates and thiocyanates to 1H,4H-selenolo[3.4-c]selenophene and 1H,4H-thieno[3,4-c]thiophene, respectively, take place by the mechanism presented in Scheme 1, and involve diallenyl diselenides and disulfides as key reaction intermediates. It is interesting to note that **33** was obtained as a solid after purification by chromatography and showed sharp methyl singlets in its proton NMR spectrum, even on peak expansion to 500 Hz. This data may

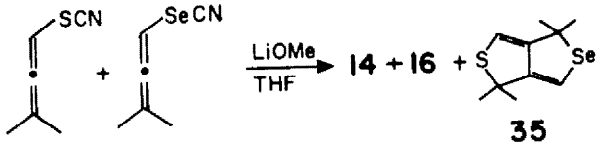
be interpreted that only one isomer, apparently the *trans*, is formed under steric control. In turn, this information may be used to rule out a concerted mechanism for the 8 π (or 12 π + n.b.) electron double Michael addition, the last step of the reaction, since the latter would require formation of both *cis* and *trans* isomers. Formation of only one isomer may thus indicate a two step process allowing the more stable isomer to be preferred. It is also interesting to compare the effect of substitution on the ease of [3,3]-sigmatropic rearrangement of the structurally related divinyl disulfides reported by Brandsma and coworkers,[27a] which in certain cases is spontaneous even at low temperature. For example, unlike the spontaneous rearrangement of β-methylvinyl disulfide **34** shown in Eq. 10, the corresponding β,β-dimethylvinyl disulfide can be isolated and does not rearrange. This result, which can also be explained on steric grounds, is also in contrast to *bis*-τ,τ-dimethylallenyl disulfide (**20**) which proceeds readily, thus indicating that further removal of the methyl groups from β- to a τ-carbon has a dramatic effect.



(10)

34

Finally, we have examined the possibility for the preparation of the novel mixed selenolo[3,4-c]thiophene **35**, starting with a mixture of **13** and **15**. Treatment of a 1:1 molar mixture of these compounds with lithium methoxide afforded a mixture **14**, **16** and **35** in a 1:1:1 molar ratio. This ratio can be explained as follows. According to Scheme 1, the ratio of the 3 observed products should also reflect the ratio of the corresponding 3 diallenyl intermediates, generated by two consecutive nucleophilic dis-



(11)

35

placements. In the first one, the methoxide ion displaces either $RS^{\ominus}$ or RSe^{-}, while in the second displacement the leaving group is the same, CN^{-}, but the heteronucleophile attacks two different heterocenters. If these two processes had the same activation energy, we might have expected the mixed diallenyl product to be formed statistically twice as much as either **20** or its diselenide analogue. However, kinetic studies by Kice and coworkers have demonstrated that selenolate anions are better leaving groups than thiolate anions,[36a] and that divalent selenium is a much more active sub-

strate than sulfur with regard to nucleophilic substitution.[3a,b] Consequently, one may expect preferential attack of methoxide on selenocyanate to liberate the selenolate anion, which in turn will prefer to react with another selenocyanate (15), thus counteracting the statistical probability mentioned above, and accounting for the observed product distribution.

EXPERIMENTAL

^{1}H NMR spectra were recorded on Varian HA 100 NMR or Varian EM-360A spectrometers in either $CDCl_3$ or CCl_4 as solvents using TMS as internal standard. Chemical shifts are reported in δ ppm units and coupling constants in Hz units. ^{13}C NMR spectra were recorded on a Varian CFT-20 spectrometer in $CDCl_3$ as solvent and using TMS as internal standard. Chemical shifts are reported in δ ppm units and coupling constants in Hz units. Infrared spectra were recorded on a Perkin-Elmer Grating Infrared spectrometer Model 457. Mass spectra were obtained on Hitachi Perkin-Elmer RMU6 Mass Spectrometer or on a Finnigan-4000 GC/MS instrument, using either electronic ionization (EI) or chemical ionization (CI).

Microanalyses were performed by Alfred Bernhardt, Microanalitisches Laboratorium, Engelskirchen, West Germany, and at the Hebrew University, Jerusalem. Solvents and reagents were purified by standard methods.

Propargyl alcohols and halides. The required propargyl alcohols, not commercially available, were prepared, by reaction of lithium acetylide with the appropriate ketone, using the general method reported by Midland.[47] Thus, reaction of monolithium acetylide with *i*-propyl ketone afforded α,α-diisopropyl propargyl alcohol in 93% yield, b.p. 67-68°/25 mm Hg; ^{1}H NMR ($CDCl_3$) δ 2.33(s,1H), 1.83 (sep, J=7Hz, 2H), 1.80 (s, 1H, disappears on addition of D_2O), 0.96 (d, J=7Hz, 6H), 0.93 (d, J=7Hz, 6H). Similarly, α-*i*-propyl-α-methylpropargyl alcohol was obtained by reaction of monolithium acetylide with methyl isopropyl ketone (yield 45%). ^{1}H NMR ($CDCl_3$) δ 2.46 (s, 1H, disappears in D_2O), 2.40 (s, 1H), 1.73 (sep, J=7Hz, 1H), 1.43 (s, 3H), 1.01 (d, J=7Hz, 3H), 0.97 (d, J=7Hz, 3H).

α,α-Diisopropylpropargyl chloride was prepared by the reaction of the corresponding alcohol with concentrated hydrochloric acid in the presence of calcium and copper chlorides, according to a general method by Hennion and Boiselle.[57] The chloride was obtained in 44% yield, b.p. 57-60°/15 mm Hg: ^{1}H NMR ($CDCl_3$) δ 2.56 (s, 1H), 2.13 (sep, 2H, J=7Hz), 1.07 (d, 12H, J=7Hz); IR (neat) 3280, 2100 cm^{-1}. α-*i*-Propyl-α-methylpropargyl chloride, prepared by the same method, was obtained in 45% yield, b.p. 30-40°/90 mm Hg:

^{1}H NMR ($CDCl_3$) δ 2.63 (s, 1H), 1.83 (sep, 1H, J=7Hz), 1.80 (s, 3H), 1.14 (d, 3H, J=7Hz), 1.13 (d, 3H, J=7Hz). α,α-Dimethyl- and α,α-dimethyl-τ-deuteriopropargyl bromides were prepared by reaction of the corresponding alcohols with PBr_3 at 0°, according to a literature procedure[48] for the first compound. α,α-Dimethyl-τ-deuteriopropargyl alcohol was prepared by reaction of the undeuteriated alcohol with excess lithium at room temperature, followed by quenching with a ten fold excess of D_2O and extraction with ether, according to a procedure previously employed in our laboratory.[39] The product was obtained in 55% yield, and its proton NMR spectrum showed only one singlet at δ 1.50.

Preparation of allenyl thiocyanates and selenocyanates. τ,τ-Dimethylallenyl and α-deuterio-τ,τ-dimethylallenyl thiocyanates (**13**, **26**) were prepared by reaction of the corresponding α,α-dimethylpropargyl bromide with sodium thiocyanate at 75° for 16 h, as previously described for the former[32] thiocyanate. The latter thiocyanate was obtained in 50% yield, b.p. 40°/0.5 mm Hg; ^{1}H NMR ($CDCl_3$) δ 1.80 (s); IR (neat) 2100, 1940 cm^{-1}.

τ,τ-Dimethylallenyl selenocyanate (**15**). To a solution of 52.3 g (363 mmole) of potassium selenocyanate in 300 mL of dry acetonitrile were added 53.4 g (363 mmole) of α,α-dimethylpropargyl bromide. The solution was stirred at room temperature for 20h, during which it became yellowish and KBr precipitated. After extraction with ether, washing with water (5x100 mL) and drying over anhydrous K_2CO_3, the solvent was removed under reduced pressure. The product was obtained as yellowish liquid with an unpleasant odor (45.7 g, 73% yield), ^{1}H NMR ($CDCl_3$) δ 5.80 (sep, J=2Hz, 1H), 1.83 (d, J=2Hz, 6H); IR (neat) 3020, 2140, 1950 cm^{-1}.

τ,τ-Diisopropylallenyl selenocyanate (**28**) was prepared from α,α-diisopropylpropargyl chloride and KSeCN, as described for **15**, except that reaction was conducted at reflux temperature(yield 70%), ^{1}H NMR ($CDCl_3$) δ 5.93 (t, J=1Hz, 1H), 2.23 (sep, J=7Hz, 2H), 1.07 (d, J=7Hz, 6H), 1.06 (d, J=7Hz, 6H); IR (neat) 3020, 2140, 1960 cm^{-1}; MS, m/e (%) (EI) 229 (M^+, 8), 123 ($C_9H_{15}^+$, 25), 81 (HSe^+, 100) 43 ($C_3H_7^+$, 80).

τ-Methyl- τ-isopropylallenyl selenocyanate (**31**) was prepared from α-methyl-α-isopropylpropargyl chloride and KSeCN, as described for **15** (yield 35%), bp 70°/0.01 mm Hg, ^{1}H NMR ($CDCl_3$) δ 5.90 (pen J=3Hz, 1H), 2.16 (sep, J=7Hz, 1H), 1.84 (d, J=3Hz, 3H), 1.10 (d, J=7Hz, 6H); IR (neat) 3020, 2140, 1950 cm^{-1}.

Thienothiophenes. 1,1,4,4-Tetramethyl-1H,4H-thieno[3,4-c]thiophene (**14**). To a solution of 736 mg (23 mmole) of methanol in 100 mL of anhydrous THF under nitrogen, were added 14.5 mL (23 mmole) of a 15% n-butyllithium solution in hexane. After 15 min of stirring at room temperature a solution of 2.875 g (23 mmole) of τ,τ-dimethylallenyl thiocyanate in 10 mL of THF was added by syringe. Stirring was continued for 8 hours at the same temperature, during which the solution became turbid and brown. Water and ether (150 mL) were then added and the ether layer washed with water (4x100 mL) and dried over anhydrous $MgSO_4$. Evaporation of the solvent at reduced pressure left a brown solid which after several washings with methanol and crystallization from the same solvent, afforded the product as white crystals (70% yield), mp 134° (d), ^{1}H NMR ($CDCl_3$) δ 5.76 (s, 2H), 1.56 (s,12H), ^{13}C NMR ($CDCl_3$) δ 31.30 (Me), 53.64 (C1 & C4) 114.68 & 151.11 (C=C); IR ($CHCl_3$) 3050, 1650 cm^{-1}; UV (EtOH) λ_{max} (ϵ_{max}) 270 (12,000), 330 (13,000) nm; MS m/e (%) (EI) 198 (M^+, 48), 183 ($M-CH_3$, 100), 150 ($M-CH_3-HS$, 80), 149 ($M-CH_3-H_2S$, 98), 135 ($M-CH_3-HS-CH_3$, 17), 134 ($M-2CH_3-H_2S$, 20). 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.

1,1,4,4-Tetramethyl-3,6-dideuterio-1H,4H-thieno[3,4-c]thiophene (27) was prepared from α-deuterio-τ,τ-dimethylallenyl thiocyanate as described for the undeuteriated compound (14) in 80% yield, mp 130° (d),, ^{1}H NMR ($CDCl_3$) δ 1.50 (s); UV (EtOH) λ_{max} 270 (12,000), 330 (13,000) nm; MS (EI), m/e 200 (M^+).

Diallenyl mono and diselenides. *bis*-τ,τ-Diisopropylallenyl diselenide (29). Method A. To a solution of 20 mg (0.6 mmole) of dry methanol in 15 mL of anhydrous THF under nitrogen, were added 0.3 mL (0.5 mmole) of a 15% *n*-butyllithium solution in hexane. After 15 min of stirring a solution of 140 mg (0.6 mmole) of τ,τ-diisopropylallenyl selenocyanate in 5 mL THF was added by syringe, followed by heating for 3h at the reflux temperature. After cooling, the product was extracted with 100 mL of ether, washed with water (3x50 mL), and dried over anhydrous K_2CO_3. Removal of the solvent at reduced pressure afforded the product as a liquid (96 mg, 80% yield).

Method B. A mixutre of τ,τ-diisopropylallenyl selenocyanate (500 mg, 2.17 mmole) and 50% H_3PO_2 (8 mL, 66 mmole) was heated at 60° for 2 h, and then worked up as described in Method A. Yield 420 mg (95%). ^{1}H NMR ($CDCl_3$) δ 6.23 (t, J=1Hz, 2H), 2.16 (m, 4H), 1.10 (d, J=7Hz, 12H), 0.98 (d, J=7Hz, 12H); IR (neat) 1940 (m) cm^{-1}; MS m/e (%) (EI) 406 (M^+, 10), 363 ($M-C_3H_7$, 30), 203 ($M-C_9H_{15}Se$, 40), 123 (C_9H_{15}, 90), 43 (C_3H_7,100).

bis-τ,τ-Diisopropylallenyl selenide (30).
A solution of *bis*-τ,τ-diisopropylallenyl diselenide (100 mg) in benzene (10 mL) was treated with tris-diethylaminophosphine (70 mg), and refluxed for 3 hours. After evaporation of the solvent, the desired product was separated by column chromatography (silica, chloroform-hexane, 2:8) in 50% yield. ^{1}H NMR ($CDCl_3$) δ 5.90 (t, J=1Hz, 2H), 2.20 (sep, J=7Hz, 4H), 1.00 (d, J=7Hz, 24H); IR (neat) 1950 (m) cm^{-1}; MS m/e (%) (EI) 326 (M^+, 18), 238 ($M-C_3H_7$, 25), 241 ($M-C_3H_7-C_3H_6$, 58), 213 ($M-2xC_3H_7-C_2H_3$, 100), 211 (51).

bis-τ-Methyl-τ-isopropylallenyl diselenide (32), was prepared by reaction of τ-isopropyl-τ-methylallenyl selenocyanate with lithium methoxide as described for 16, except that the reaction was conducted for 14 h at room temperature. The product was obtained as a liquid (65% yield), containing about 30% of the cyclization product. ^{1}H NMR ($CDCl_3$) δ 6.06 (pen, J=2Hz, 2H), 2.26 (sep, J=7Hz, 2H), 1.73 (d, J=2Hz, 6H), 1.03 (d, J=7Hz, 12H).

Seleno[selenophenes. 1,1,4,4-Tetramethyl-1H,4H-selenolo[3,4-c]selenophene (16). Method A. This procedure was exactly the same as that used for the corresponding thienothiophene except for the use of τ,τ-dimethylallenyl selenocyanate instead of thiocyanate and an extra 7 hours of stirring at room temperature. The product (65% yield) was obtained as a white solid which was crystallized from methanol. Mp 127-128.5°. Method B - A mixture of 2.0 g (12 mmole) of τ,τ-dimethylallenyl selenocyanate and 36 mL (330 mmole) of a 50% H_3PO_2 solution was heated at 60° for 2 h. After cooling to room temperature, the product was extracted with ether as usual. Removal of the solvent at reduced pressure afforded 1.7 g (94% yield) of the desired product. ^{1}H NMR ($CDCl_3$) δ 6.36 (s, 2H), 1.70 (s, 12H); IR ($CHCl_3$) 3080, 1670 cm^{-1}; UV (EtOH) λ_{max} 335 (ε=18,000); MS m/e (%) (EI) 294 (M^+, 80), 279 ($M-CH_3$, 80), 198 ($M-CH_3-HSe$, 100), 197 ($M-CH_3-H_2Se$, 85), 183 ($M-CH_3-HSe-CH_3$, 40). Calcd. for $C_{10}H_{14}Se_2$: C, 41.09; H, 4.79; Se, 54.09. Found: C, 41.00; H, 4.72; Se, 53.87.

1,4-Diisopropyl-1,4-dimethyl-1H,4H-selenolo[3,4-c]selenophene (33). Method A. A mixture of *bis*-τ-isopropyl-τ-methylallenyl diselenide and its cyclization product in the ratio of 7:3 (100 mg), dissolved in 20 mL of acetonitrile was refluxed for one hour. Removal of the solvent at reduced pressure, followed by column chromatography (silica, pentane) afforded the desired product as a white solid, which was quite sensitive as neat, and was therefore stored in chloroform Method B was the same as for the

preparation of the tetramethyl analogue except for the use of τ-isopropyl-τ-methylallenyl selenocyanate (500 mg, 2.5 mmole) substrate and heating for 9 hours. The product (275 mg) was obtained in 65% yield. ^{1}H NMR ($CDCl_3$) δ 6.20 (s, 2H), 2.00-1.50 (m. 2H), 1.66 (s, 6H), 0.90 (d, J= 7Hz, 12H); IR (neat) 3040, 1660 cm^{-1}; UV (EtOH) λ_{max} 336 nm (ε=15,000); MS m/e (%) (EI) 350 (M^+, 100), 307 (M-C_3H_7, 90), 226 (M-C_3H_7-HSe-CH_3, 90), 210 (M-C_3H_7-H_2Se-CH_3, 70), 183 (M-2xC_3H_7-HSe, 30), 182 (M-2xC_3H_7-H_2Se, 30).

1,1,4,4-Tetramethyl-1H,4H-selenolo[3,4-c]thiophene (35), was prepared by treatment of a 1:1 mixture of τ,τ-dimethylallenyl selenocyanate and thiocyanate with lithium methoxide, as described for the thienethiopehne analogue, except that stirring was continued for 20 hours. The product was obtained together with the corresponding thienothiophene (14) and selenoloselenophene (16) analogues in the ratio of 1:1:1, as evidenced by the NMR and GC data (yield 50%). The mixture was separated by gas chromatography using a 10% SE-30 on chrom. W 3 meter long column, at 120° column and injection block temperature, and 160° detector temperature. Rate of flow was 1 mL per second and retention times were 42, 60 and 87 min for the thienothiophene, selenothiophene and selenoloselenophene, respectively. Using 0.2 g of the mixture, 70 mg of 35 were thus obtained, Mp 126.5-127.5°, ^{1}H NMR ($CDCl_3$) δ 6.30 (bs, 1H), 5.96 (bs, 1H), 1.70 (s, 6H), 1.56 (s, 6H); MS m/e (%) (EI) 246 (M^+, 52), 231 (M-CH_3, 63), 198 (M-CH_3-HS, 24), 197 (M-CH_3-H_2S, 22), 183 (M-2xCH_3-HS. 26), 182 (M-2CH_3-H_2S, 26), 150 (M-CH_3-HSe, 90), 149 (M-CH_3-H_2Se, 100), 135 (M-2CH_3-HSe, 49), 134 (M-2CH_3-H_2Se, 34).

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