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Intramolecular Homolytic Substitution at Tellurium: Preparation of a Dihydrotellurophene by Alkyltelluride-Mediated $S_{RN}1$ / S_Hi Reactions

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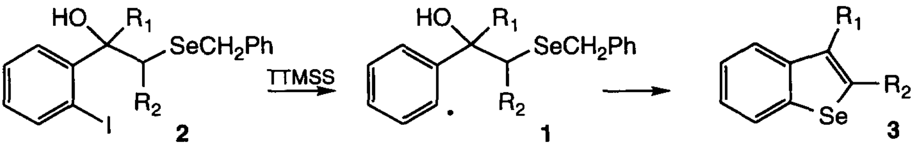
Abstract: Reaction of 1-methyl-1-(2-iodophenyl)oxirane (**4**) with two equivalents of sodium butyltelluroate (NaTeBu), generated throught the sodium borohydride reduction of dibutylditelluride, in THF, affords 2,3-dihydro-3-hydroxy-3-methylbenzo[b]tellurophene (**6**) in 57% yield, together with 1-(butyltelluro)-2-phenyl-2-propanol (**7**, 7%). This transformation presumably involves a tandem $S_{RN}1$ / S_Hi sequence which was investigated further through the reactions of 1-(benzylseleno)-2-phenyl-2-propanol (**2**, R_1 = Me; R_2 = H) and 1-allyloxy-2-iodobenzene (**9**) with sodium butyltelluroate under similar conditions. Mechanistic and kinetic implications are discussed. © 1997 Elsevier Science Ltd.

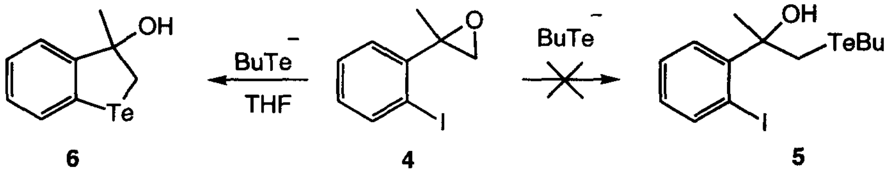
Recently, we reported that aryl radicals (**1**) derived from iodides (**2**) through reaction with tris(trimethylsilyl)silane (TTMSS/AIBN) in benzene react to afford benzoselenophenes (**3**) in good yields.[1] These transformations presumably involve intramolecular homolytic substitution at the selenium atom in (**1**) with expulsion of the benzyl radical as the key ring-forming step in the overall mechanism (Scheme 1).

Scheme 1



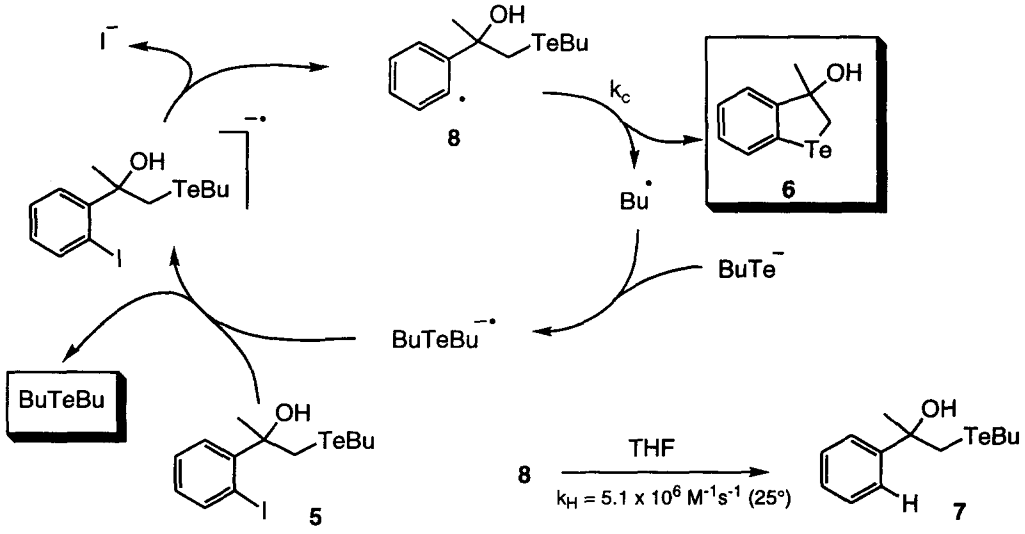
With the aim of expanding synthetic methodology involving homolytic substitution, we began to explore the analogous chemistry involving tellurium with the aim of preparing benzotellurophenes. Accordingly 1-methyl-1-(2-iodophenyl)oxirane (**4**) was reacted for 24h with two equivalents of sodium butyltelluroate,[2] generated by the reduction of dibutylditelluride[3] with sodium borohydride in THF followed by the addition of a small quantity of methanol.[4] ^1H NMR Spectroscopy of the crude reaction mixture revealed the absence of starting material (**4**), while ^{125}Te NMR spectroscopy revealed the presence of dibutylditelluride (δ 225.9),[5] dibutyltelluride (δ 110.5)[5] and a third signal at δ 418.0 which presumably corresponded to the major (TLC) product. To our surprise, none of the expected telluride (**5**) was isolated from the reaction mixture by flash chromatography, rather the major product was determined to be 2,3-dihydro-3-hydroxy-3-methylbenzo[b]tellurophene (**6**) which was isolated in 57% yield, together with a small quantity (7%) of 1-(butyltelluro)-2-phenyl-2-propanol (**7**) (Scheme 2).

Scheme 2



Presumably tellurophene (**6**) arises via intramolecular homolytic substitution at the tellurium atom in radical (**8**) with expulsion of butyl radical. The aryl radical (**8**) is presumably generated as part of a butyltelluride mediated $S_{RN}1$ chain mechanism[6] (Scheme 3) which relies on the rapid generation of telluride **5**, *in situ*. The minor quantities of reduced product (**7**) isolated are most likely to arise via hydrogen abstraction by aryl radical (**8**) from the tetrahydrofuran solvent and support the view that **5** is generated *in situ*. To the best of our knowledge, the transformation depicted in Scheme 3 represents the first example of intramolecular homolytic substitution at tellurium atom.

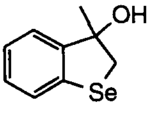
Scheme 3



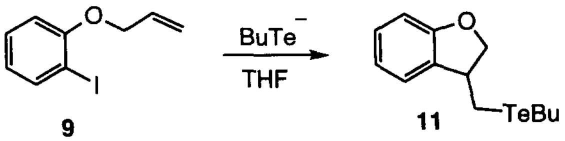
In order to establish the intermediacy of aryl radicals in these reactions, we examined the reaction of the benzylselenide (**2**; R_1 = Me, R_2 = H) as well as 1-allyloxy-2-iodobenzene (**9**) with one equivalent of sodium butyltelluroate in THF under the previously described conditions. To our delight, after 24h, **2** (R_1 = Me, R_2 = H) had been completely consumed. Apart from small amounts of unidentifiable material, ^{1}H NMR spectroscopy indicated that **2** had been transformed predominantly into 2,3-dihydro-3-hydroxy-3-methylbenzo[b]selenophene (**10**) which was isolated in 74% yield after careful flash chromatography.

In contrast, the reaction involving **9** was only 50% complete after 24h. ^{1}H NMR spectroscopy of the crude reaction mixture indicated the presence of only starting material (**9**, 50%) and ring-closed material (**11**, 50%). Telluride (**11**) appeared to be unstable and could only be isolated in 24% yield as a crystalline solid after flash chromatography. Crich and coworkers recently reported similar stability problems with structurally related phenyl tellurides.[7] It is interesting to note that Beckwith and Palacios reported similar intramolecular homolytic addition during $S_{RN}1$ sequences involving PhS^- and Ph_2P^-.[8]

The preparation of **10** and **11** from precursors **2** (R_1 = Me, R_2 = H) and **9** respectively leave no doubt about the intermediacy of aryl radicals and the involvement of the $S_{RN}1$ mechanism in the chemistry described above.



10

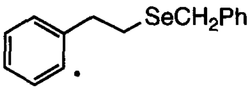


9 **11**

The observed product distribution in the ring-closure of radical (**8**) allow, for the first time, an estimate for the rate constant for intramolecular homolytic substitution at tellurium atom. Application of the appropriate integrated rate expression[1] (eqn. 1), which integrates to eqn. 2 under pseudo first-order conditions in THF, and given that [THF] = 12 M,[9] that [**6**] / [**7**] = 57/7 = 8.14 and, that the rate constant for abstraction of hydrogen atom by aryl radical from THF (k_H) is $5.1 \times 10^6\ M^{-1}s^{-1}$ at 25°,[10] the rate constant for ring-closure of **8** (k_c) can be determined to be approximately $5 \times 10^8\ s^{-1}$ at 25°. This value is to be compared with the estimated rate constant for the similar ring-closure at selenium atom in selenide (**12**) with expulsion of benzyl radical, which is estimated to be approximately $3 \times 10^7\ s^{-1}$ at 80°.[1] The increase in the rate constant for the ring-closure of **8** over **12** is expected on the basis of well established trends in the rate constants for intermolecular homolytic substitution at selenium and tellurium and relative leaving group abilities.[11]

$$d[\mathbf{6}]/d[\mathbf{7}] = k_c/(k_H[THF]) \qquad \text{......(eqn 1)}$$

$$[\mathbf{6}]/[\mathbf{7}] = k_c/(k_H[THF]) \qquad \text{......(eqn 2)}$$



12

13 **14**

In order to assess the validity of the above approach, we applied the same procedure to the ring-closure of the aryl radical derived from the iodide (**9**). Recognising the cleanness of this reaction and assuming that ^1H NMR spectroscopy has a 1% detection limit (ie. [**11**]/[**14**] > 99), a rate constant for the cyclization of radical (**13**) can be estimated to be greater than approximately $6 \times 10^9\ s^{-1}$ at 25°, consistent with the well-established value of $6.3 \times 10^9\ s^{-1}$ (30°).[10]

It is interesting to note that when dibutylditelluride was replaced with diphenylditelluride in the above reactions, no products of $S_{RN}1$ - type chemistry were observed. Indeed the only product of reaction appears to be diphenylditelluride and starting iodide. We have previously noted that sodium phenyltelluroate appears to undergo rapid oxidation in the presence of some classes of aromatic substrate.[12]

Acknowledgments

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