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NEW BRIDGES IN [2.2]PARACYCLOPHANES: THE INTERACTION OF CHALCOGENIDE HALIDES WITH *PSEUDO-GEMINAL* TRIPLE BONDS

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Abstract *Novel heteroatom containing bridges have been introduced in [2.2]paracyclophanes by the interaction of chalcogenide halides with* pseudo-geminal *triple bonds. The* anti-*addition with Markovnikov orientation of selenium halides to 4,15-bisethynyl[2.2]paracyclophane leads to the corresponding* E-*adducts. The interaction of* pseudo-geminally *substituted bispropargylic alcohols with disulfur dichloride and sulfur dichloride leads to a mixture of cyclic ethers. These compounds are formed under mild acidic conditions provided by the organic ammonium chlorides or silica gel. The corresponding dipropargyloxy sulfides have been identified as reaction intermediates.*

Supplemental materials are available for this article. Go to the publisher's online edition of Phosphorus, Sulfur, and Silicon and the Related Elements *to view the free supplemental file.*

Keywords [2.2]Paracyclophanes; selenium electrophiles; sulfur electrophiles

INTRODUCTION

The sigmatropic rearrangements of allylic and propargylic esters of sulfur acids at various oxidation states have proven to be a rich source of synthetically valuable and mechanistically intriguing reactions, often yielding novel and surprising products.[1,2] However, due to the rigid molecular framework provided by the paracyclophane unit and its short inter-annular distance, functional groups in *pseudo-geminally* substituted [2.2]paracyclophanes are often held in such a position as to allow highly specific reactions to take place between them. In one such application, unsaturated cyclophane bisesters undergo intramolecular photocyclization to the corresponding ladderane isomers.[3–5] In view of our past experience with the use of electrophilic sulfur reagents with hydroxyalkynes,[6] we decided to investigate the reactivity of the chalchogenide halides towards 4,15-bisethynyl[2.2]paracyclophane and *pseudo-geminally* substituted propargylic alcohols.

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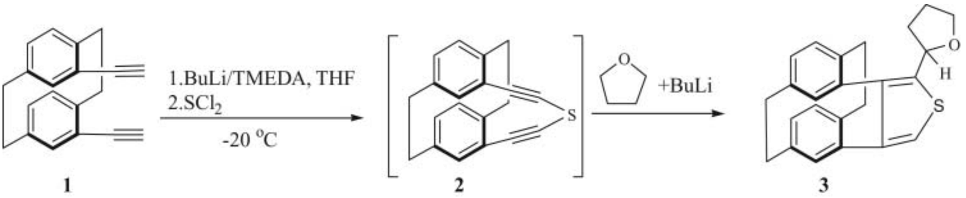
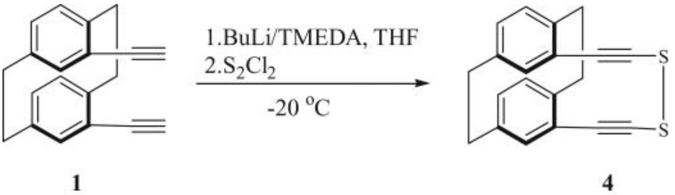
RESULTS

Preliminary investigations have shown that the reaction of *pseudo-geminal* bis-ethynyl[2.2]paracyclophane **1** with *n*-BuLi in THF followed by treatment with SCl_2 resulted in the formation of thiophene substituted paracyclophane derivative **3** (Scheme 1).[7] Most likely the cycloaromatization is induced by a nucleophilic attack of THF-anion on one of the acetylenic carbon atoms of the intermediate unstable sulfide **2**.



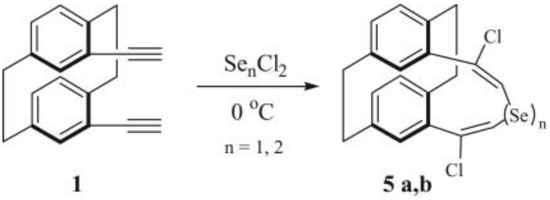
Scheme 1

Under the same reaction conditions, the treatment of bisacetylene **1** with monosulfur monochloride leads to the corresponding disulfide **4**, in 65% isolated yield (Scheme 2). The stability of this compound could be explained by a less hindered structure—that of the monosulfide **2**—and the lack of cycloaromatization.



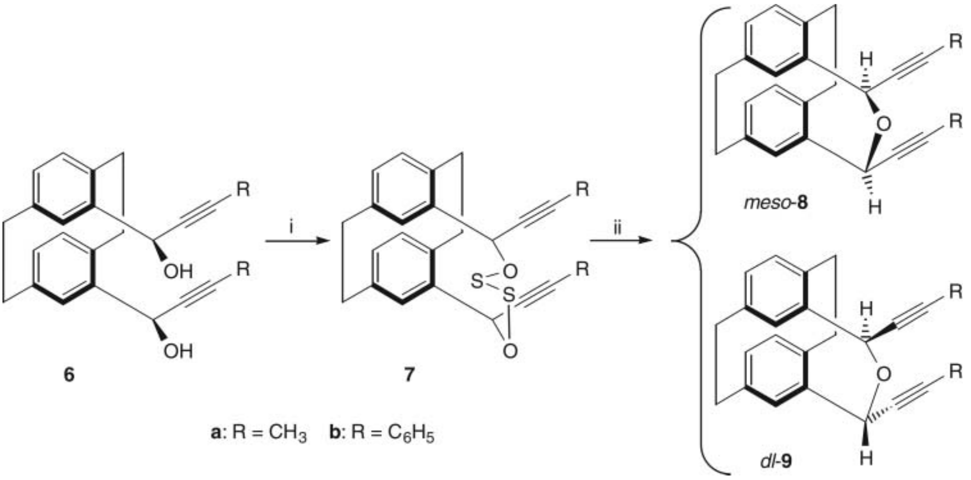
Scheme 2

Prompted by the simple and efficient recent preparation of selenium dichloride from elemental selenium and sulfuryl chloride,[8] we have investigated the reaction of *in situ* prepared $SeCl_2$ with *pseudo-geminal* bis-ethynyl[2.2]paracyclophane **1** (Scheme 3, n = 1). Molecular modeling and preliminary analytical data have indicated that *anti*-addition with Markovnikov orientation takes place. The addition of monoselenium monochloride proceeds in a similar manner (Scheme 3, n = 2), leading to diselenide **5b**. In both cases, the addition of electrophilic selenium reagents to bis-ethynyl[2.2]paracyclophane produced preferably the corresponding *E*-adducts.



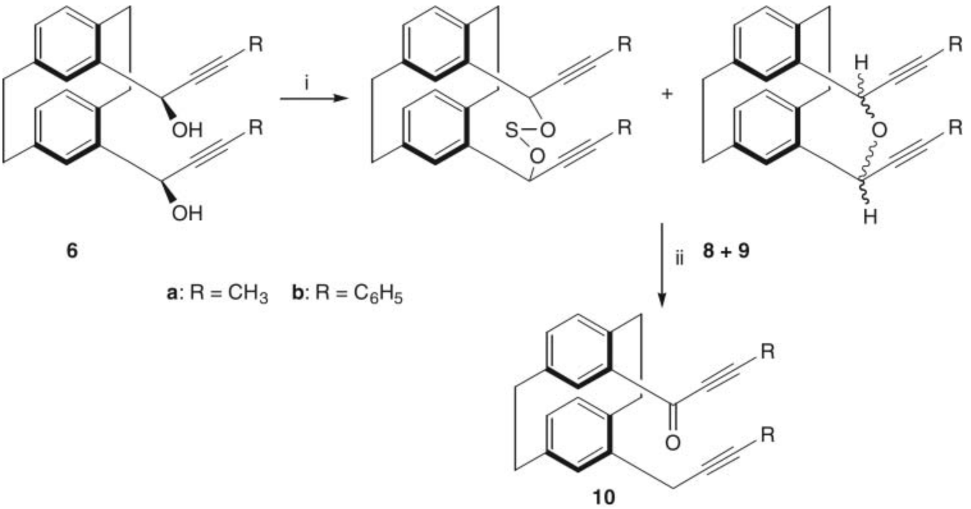
Scheme 3

The interactions between *pseudo-geminally* substituted bispropargylic alcohols **6** and sulfur chlorides have been studied under various experimental conditions. The dipropargyloxy disulfides **7** have been demonstrated as reaction intermediates of monosulfur monochloride. Under mild acidic conditions provided by $Et_3N{\cdot}HCl$ or silica, these compounds undergo sulfur elimination, providing a mixture of *meso*-**8** and *d,l*-**9** cyclic ethers in a 2.5:1 ratio (Scheme 4).



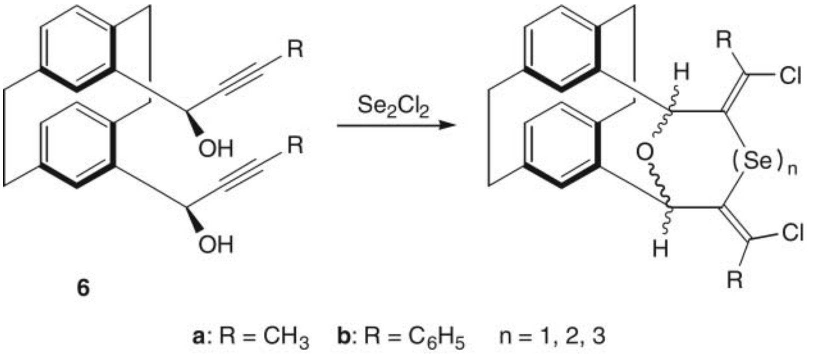
Scheme 4 Conditions: (i) S_2Cl_2, NEt_3 (2 eq.), Et_2O, –78°C; (ii) silica gel.

The sulfur dichloride has provided dipropargyloxy sulfides, compounds that were found to be responsible for a vinylogous pinacol rearrangement (Scheme 5).



Scheme 5 Conditions: (i) SCl_2, NEt_3 (2 eq.), CH_2Cl_2, –78°C; (ii) silica gel.

The regio- and stereospecific addition of monoselenium monochloride to *pseudo-geminally* substituted bispropargylic alcohols was performed under high dilution conditions. The disproportionation reaction of selenium monochloride to selenium dichloride and triselenium dichloride leads to the corresponding divinylic mono- and triselenides (Scheme 6). The stereochemistry of the newly generated double bond was assigned as *Z* by 2D NMR experiments.[9] The *syn* addition of selenium electrophiles appears to be directed by hydroxyl groups.



Scheme 6

EXPERIMENTAL

Disulfur dichloride and diselenium dichloride was purchased from commercial sources. Sulfur dichloride was prepared according to data in the literature[10] and distilled prior to use in the presence of phosphorus trichloride. Analytical data are presented in the Supplemental Materials (available online).

Reaction of Disulfur Dichloride with Bisacetylene 1

To a solution of bisacetylene **1** (128 mg, 0.5 mmol) and tetramethylethylenediamine (0.15 mL, 1 mmol) in anhydrous THF (100 mL), a solution of *n*-BuLi (1.6 M, 0.65 mL, 1.05 mmol) was added dropwise at –20°C. The reaction mixture was stirred at this temperature for 30 min, and then S_2Cl_2 (0.04 mL, 0.5 mmol) in anhydrous THF (50 mL) was added dropwise. After 2 h at this temperature, the mixture was poured into water and extracted with methylene chloride. After the usual workup, evaporation of the solvent gave the crude product as brown viscous oil. Purification by column chromatography on silica gel using CH_2Cl_2/pentane 1:1 as eluent provided disulfide **4** (100 mg) in 65% isolated yield.

Reaction of Selenium Halides with Bisacetylene 1 and Bispropargylic Alcohols 6: Typical Procedure

To a solution of bisacetylene **1** (128 mg, 0.5 mmol) in CH_2Cl_2 (100 mL), a solution of Se_2Cl_2 (0.042 mL, 0.5 mmol) in CH_2Cl_2 (50 mL) was added dropwise at 0°C. The reaction mixture was allowed to warm up to room temperature and then stirred at this temperature for 8 h. The solvent was removed under vacuum, and the residue was purified by PTLC using CH_2Cl_2/pentane (1:1) as eluent to give diselenide **5b** (53 mg) in 22% isolated yield.

Reaction of Disulfur Dichloride with Bispropargylic Alcohols 6: Typical Procedure

To a solution of bispropargylic alcohol (**6a**, 86 mg, 0.25 mmol) in diethyl ether (30 mL), triethyl amine (0.07 mL, 0.5 mmol) was added and the reaction mixture was cooled to –78°C. A solution of disulfur dichloride (0.02 mL, 0.25 mmol) in diethyl ether (15 mL) was added dropwise. After 1 h, the reaction mixture was allowed to warm to room temperature and stirred for an additional 2 h. After the usual work-up (H_2O, $NaHCO_3$, $MgSO_4$), evaporation of the solvent gave the crude product as a brown viscous oil (92 mg). NMR data of dipropargyloxy disulfide **7a** were selected from the spectrum of this oil. Purification by column chromatography on silica gel using CH_2Cl_2/pentane 1:1 as eluent provided *meso*-ether **8a** and *d,l*-ether **9a** in a 2.5:1 ratio.

Reaction of Sulfur Dichloride with Bispropargylic Alcohols 6: Typical Procedure

To a solution of bispropargylic alcohol (**6a**, 172 mg, 0.5 mmol) in CH_2Cl_2 (700 mL), triethyl amine (0.14 mL, 0.5 mmol) was added and the reaction mixture was cooled to –78°C. A solution of sulfur dichloride (0.032 mL, 0.5 mmol) in CH_2Cl_2 (50 mL) was added dropwise. After 1 h, the reaction mixture was allowed to warm up to room temperature and stirred for an additional 2 h. After the usual work-up (H_2O, $NaHCO_3$, $MgSO_4$), evaporation of the solvent gave the crude product that was purified by column chromatography on silica gel using CH_2Cl_2/pentane 1:1 as eluent. The pinacolone **10a** was obtained as white crystals (100 mg, 61%).

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