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Adaptation of the Photo-Induced [1,3]-Allylic Phenylthio Shift to the Preparation of Functionalized Diquinanes

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Abstract: The feasibility of utilizing the little known photo-induced [1,3]-allylic phenylthio shift in the context of functionalized diquinane construction has been tested.

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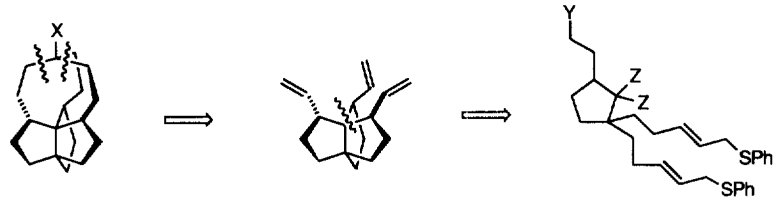
The capped propellane **1** is an attractive synthetic target because of its unique topology and the prospect that its ionization might give rise to the first σ-allyl cation [1,2]. From the retrosynthetic perspective, we have viewed the stereochemically defined trivinyl substituted hydrocarbon **2** to be a potentially suitable precursor to **1** [3]. These considerations warrant that a protocol be developed for the convenient mutual fusion of cyclopentane rings with proper allowance for precise positioning of the vinyl substituents. A significant advance can be contemplated if a functionalized cyclopentane such as **3** was to be made available. Geminal introduction of the allylic sulfide residues as shown, together with incorporation of the potential radical-initiating substituents Z, could prove suitable to operation of a useful two-fold cyclization process. S_H2' ring closures of this type involving carbon-centered radicals are precedented [4,5], and a number of Z groups were considered suitable [6]. Beyond these



1 **2** **3**

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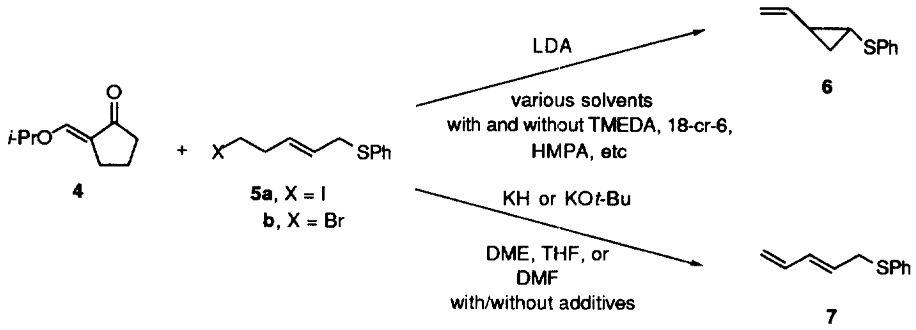
considerations, the deployment of this tactic in the present context has necessarily been augmented by the first application of the little known photo-induced [1,3]-allylic phenylthio shift [7] in a synthetic setting.

The regiochemical control offered by the latter rearrangement emerged as critical when attempts to alkylate the lithium or potassium enolates of **4** [8] directly with **5a** [5a] or **5b** [9] (both prepared by modification of Tilak's original procedure [10]) gave only the elimination products **6** and **7**, respectively, even at -60 °C (Scheme 1). The generality of this result can be attributed to the homoallylic nature of **5a** and **5b**. To avoid this feature, the known alcohol **8** [5b] was transformed into iodide **9** in advance of coupling with the potassium salt of **4** (Scheme 2). This was a critical experiment in that twofold alkylation had necessarily to proceed more rapidly than proton transfer to generate a transient allyl anion. In the case at hand, the use of DMF as solvent and a reaction temperature of -40 °C gave the desired **10** as a mixture of diastereomers.

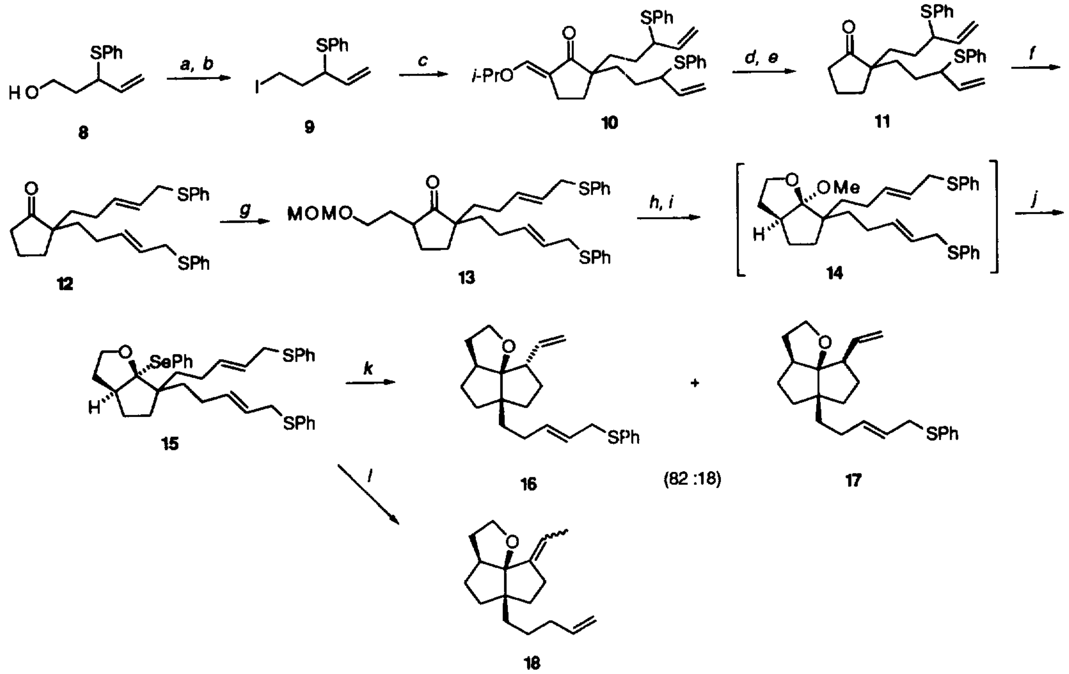
Scheme 1



With this chemistry developed, it proved a relatively simple matter to effect conversion to **11** by sequential hydrolysis in cold 6M hydrochloric acid and heating (ca 120 °C) with 20% sodium carbonate solution [11]. The isomerization of **11** to **12** was smoothly accomplished in 70% yield by irradiation with a 275W sunlamp. Purification was routinely carried out at this point, and no evidence was obtained for the competitive formation of *Z* isomers.

The most convenient way uncovered for the attachment of a two-carbon side chain at C-5 involved alkylation of the lithium enolate of **12** with the MOM ether of 2-iodoethanol. With arrival at **13**, it was now possible to unmask the primary hydroxyl group in preparation for intramolecular cyclization in the form of acetal **14**. Conversion of this intermediate to **15** required only stirring with tris(phenylseleno)borane [12] in $CHCl_3$ at room temperature. As a consequence of the existence of considerable steric shielding at the reaction center, the efficiency of the two step conversion (44%) was modest, although acceptable. Attempts to generate bis(phenylseleno) acetals [13] from **13** and analogs thereof carrying different two-carbon side chains were to no avail, even when recourse was made to higher temperature (110 °C) and pressures (15 kbars).

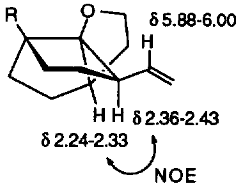
Scheme 2



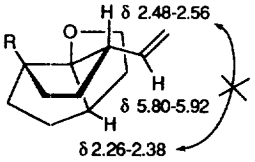
^{a} TsCl, py, rt (73%). ^{b} NaI, HMPA, rt (98%). ^{c} KO*t*-Bu, DMF, -40 °C, 50 min (43%). ^{d} 6 M HCl, THF, 0 °C, 1 h. ^{e} 20% Na_2CO_3 in H_2O, reflux, 7 h (72% for two steps). ^{f} hv, 275W sunlamp, CCl_4, 10 h (70%). ^{g} LDA, THF-HMPA; $I(CH_2)_2OMOM$ (38%). ^{h} 6 M HCl, THF-MeOH (1:1), reflux (76%). ^{i} $HC(OMe)_3$, TsOH, MeOH, Δ, 2 h. ^{j} $B(SePh)_3$, $CHCl_3$, rt, 14 h (44% for 2 steps). ^{k} $(TMS)_3SiH$, AIBN, toluene, 90 °C, 1 h (80%). ^{l} Bu_3SnH, AIBN, toluene, Δ (77%).

It was therefore of interest to explore different methods for the intramolecular free radical cyclizations of **15**. Two are detailed here. With the precedent of Giese [14] in mind, we first examined the use of tris(trimethylsilyl)silane [15] in toluene at 70-90 °C with AIBN as the initiator. It was interesting to find that **16** and **17** were formed in a combined yield of 80%. That the desired α-isomer was formed preferentially (82:18) was established by NOE studies (see **A** and **B**). This product distribution appears to be the result of kinetic control, since MM2 calculations using the MODEL KS 2.96 program indicated **C** and **D** to be closely comparable in energy [16].

In contrast to the above, recourse to tri-*n*-butyltin hydride and AIBN in refluxing toluene proved to be too harsh. As seen in **18**, not only did the vinylic double bond migrate, but the second phenylthio substituent was reductively eliminated. Nevertheless, the feasibility of producing **16** serves as a positive indicator of the workability of this methodology [17].



A



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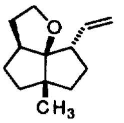

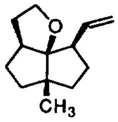

	C	D
ΔE_{strain}	21.1 kcal/mol	21.2 kcal/mol
ΔH_f	-46.0 kcal/mol	-45.9 kcal/mol
ΔE_{total}	32.95 kcal/mol	33.03 kcal/mol

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[16] We thank Dr. Eugene Hickey for these calculations.

[17] All new compounds described herein exhibited IR, ^{1}H NMR, ^{13}C NMR, and MS spectral/combustion data in satisfactory agreement with the assigned structures.