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Thallium Ion Mediated Ring Expansion of 1-Trimethylsilyloxy-1-alkenylcycloalkanes to α-*exo*-Methylenecycloalkanones

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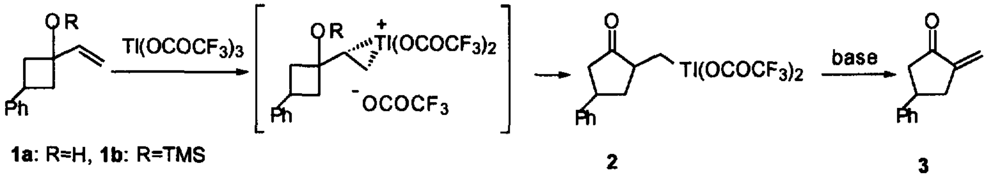
Abstract: Treatment of TMS ethers of 1-alkenyl-1-cycloalkanols with thallium trifluoro acetate in acetonitrile affords the ring expanded α-exo-methylenecycloalkanones.

Oxythallation of alkenes with thallium(III) acetate, a reaction which closely resembles the well-known oxymercuration, is a simple and unique method for the direct preparation of organothallium compounds. Organothallium compounds constitute very useful intermediates in organic synthesis because they can be produced with a high degree of regio- and stereoselectivity, and, because the thallium moiety undergoes facile substitution by various other functional groups.[1] In connection with our continuing interest in ring expansion reactions,[2] our attention was focused on how thallium ion mediated ring expansion of 1-alkenyl-1-cycloalkanols might differ from mercurinium ion mediated ring expansions.[3] We envisioned that the cationic species ($Tl(CF_3COO)_2^+$), generated from thallium(III) trifluoroacetate (TTFA), would undergo an electrophilic attack on the carbon-carbon double bond generating a thallium intermediate, which would subsequently rearrange to the ring-expanded cyclic ketone having α-*exo*-methylene group as shown in Scheme 1.

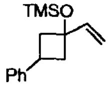
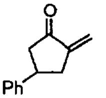
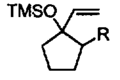
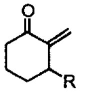
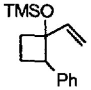
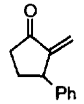
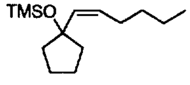
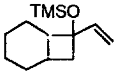
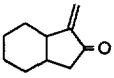
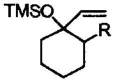
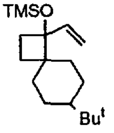
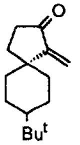
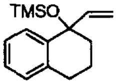
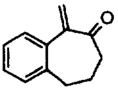


Scheme 1

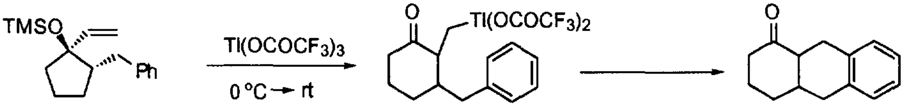
Treatment of **1a** with TTFA in acetonitrile at room temperature resulted in the slow consumption of the starting material. The resulting product, α-methylencyclopentanone (3), was isolated in 72% yield after 16 h. When the reaction was carried out in dichloromethane or tetrahydrofuran, lower yields were realized, yielding the desired product in 57% and 61% yield, respectively. Furthermore, repeating the reaction in acetonitrile under the same conditions using an equimolar mixture of TTFA and triethylamine gave **3** in only 31% yield along with the recovery of **1a** (57%).

To solve the problem of strongly acidic conditions, the hydroxy group of **1a** was trimethylsilylated to give **1b**. The use of the substrate **1b** gave much better result, yielding **3** in 82% yield, after treatment with aqueous sodium bicarbonate. The remaining reactions were, therefore, carried out with 1-trimethylsilyloxy-1-alkenylcycloalkanes in acetonitrile. Table 1 summarizes some experimental results and illustrates the efficiency and scope of the present method. The ring expansion of 4-membered ring systems was complete within 30 min, whereas that of 5- and 6-membered ring systems required 2 h for completion of the reaction. Most of the substrates with exception of entries 6 and 7 derived from cyclic ketones underwent ring expansion reactions, yielding synthetically important α-exo-methylenecycloalkanones in good yields. Although ring expansion proceeded smoothly in entry 5, it is somewhat surprising that the reaction did not occur in the case of entries 6 and 7. It has been reported that the kinetic effect of olefin structure on the rate of oxythallation decreases in the order of isobutene>but-1-ene, propylene>but-2-ene>ethylene.[4] It is, therefore, assumed that ring expansion did not take place because of the relatively low reaction rate of the but-2-ene type olefin structure in the molecules. In entry 7, even though the more reactive vinyl group was

Table 1. Synthesis of α-methylenecycloalkanones

entry	substrate	product	yield (%)[a]	entry	substrate[b]	product	yield (%)[b]
1			82%	5			84%
2			92%	6			no reaction
3			73%	7			no reaction
4			93%	8			74%

[a] isolated yields [b] R=n-C_9H_{19}



4 (*cis/trans*=9:1) **5** **6** (*cis/trans*=9:1) 70%

introduced in a six-membered ring, ring expansion did not take place. This is probably due to insufficient energy compensation for the larger ring strain energy in the seven-membered ring and the low migratory aptitude of the secondary carbon in the ring. Alternatively, when an aromatic ring, having much better migratory aptitude than the secondary carbon, was inserted at the C-2 and C-3 position of six-membered ring system (entry 8), the ring-expansion reaction occurred smoothly. Furthermore, when **4** was treated with TTFA in acetonitrile for 2 h, **6** was obtained in 70% yield as a result of participation of the benzene ring via intramolecular assistance.

As compared with mercurinium mediated ring expansion reaction,[3] the present method is less efficient and works well only with 4-membered ring systems, indicating that the thallium intermediates are much less reactive than mercurinium ion intermediates. Furthermore, it is noteworthy that the thallium mediated reaction underwent electrophilic aromatic substitution in **5**, whereas the mercurinium mediated reaction did not undergo the same type of the reaction.[5]

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References and Notes

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5. A typical procedure is as follows. The substrate **1b** (88mg, 0.36 mmol) was added to a solution of TTFA (170 mg, 0.40 mmol) in acetonitrile (5 ml) and the reaction mixture was stirred at room temperature for 30 min, quenched with saturated aqueous $NaHCO_3$ and extracted with ether. The organic layer was washed with brine, dried, and evaporated to dryness. The crude product was purified by silica gel column chromatography to give **3** (45 mg, 82%).

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