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Amberlyst 15-Catalyzed Cyclizations of Propargylic Silanes

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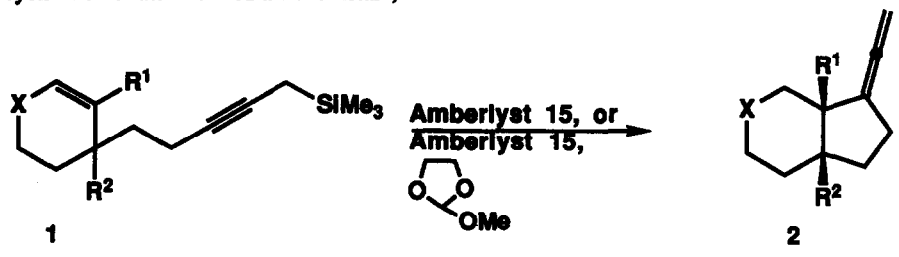
Abstract: A very efficient and simple route to bicyclic ketones using propargylic silanes is described. The cyclization is initiated by a trace of Amberlyst 15 that is added to a reaction vessel. Stirring at room temperature and non-aqueous work-up yielded several bicyclic ketones in high chemical yields containing the synthetically very useful terminal allene.

Intramolecular Sakurai reactions have shown to be very useful transformations to construct various ring sizes in annulation reactions in a stereospecific way.[1-4]

These reactions are initiated either by Lewis acids or fluoride ion.[1-4] The use of Brønstedt acids works with ene-ketals; [5] enones containing allylic silanes generate only protodesilylation products.[6] The novel process we describe here uses the resin[7,8] Amberlyst 15 as a proton source in order to catalyze a powerful new cyclization using propargyl silanes as terminating groups. This technique uses a catalytic amount of Amberlyst 15 to promote a very efficient cyclization as an alternative to other initiators described earlier. The reaction demonstrates a very useful and simple way to construct bicyclic ketones - in higher chemical yield than Lewis acid-mediation - containing a terminal allene and two quartenary centers that are set up in a one-pot procedure.

The starting materials **1** are obtained by our methods described earlier, using vinylogous esters as building blocks.[9,10] A direct cyclization of enones **1** in the presence of Amberlyst 15 generates ketones **2** in high chemical yield. [11,12] In the presence of methoxy dioxolane the desired ketals **2** are obtained in very high yield (probably by a cyclization of the intermediate ene-ketal[5]).



1 **2**

Yield: X=  **, R^1= H, R^2= Me: 85%; R^1= Me, R^2= Me: 80%**

Yield: X=  **, R^1= H, R^2= Me: 90%; R^1= Me, R^2= Me: 84%**

In contrast to our earlier procedures, this new technique is easy to use and makes intramolecular additions of propargyl silanes even more attractive in comparison to classical Michael additions.

In summary, we have shown that additions of propargylic silanes to enones or ene-ketals can be run in a sim-

ple fashion using a two phase system in the presence of a mild acid source. A non-aqueous work-up and room temperature conditions makes this novel cyclization technique very attractive for sensitive cyclization subtrates.

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References and Notes

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2. Majetich, G.; Hull, K.; Lowery, D.; Ringold, C.; Defauw, J. in *Selectivities in Lewis Acid-Promoted Reactions*; Schinzer, D., Ed.; Kluwer Academic Publishers Group: Dordrecht, Holland; 1989.
3. Majetich, G. "Allylsilanes in Organic Synthesis", in *Organic Synthesis, Theory and Applications*, Hudlicky, T., Ed.; Jai Press, Inc.: Greenwich, CT, 1989; pp 173-240.
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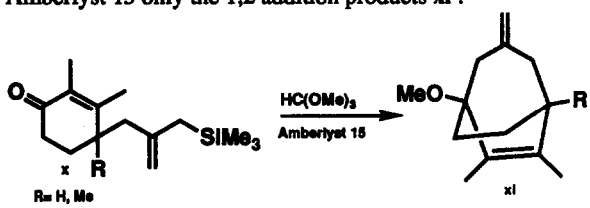
6. Note added in proof: The allylsilanes **x** yielded under trans-ketalization conditions in the presence of Amberlyst 15 only the 1,2 addition products **xi** :



7. Majetich, G.; Khetani, V. *Tetrahedron Lett.* **1990**, 31, 2243.
8. Commercially available Amberlyst 15 resin was used (SERVA, Fine Chemicals, Heidelberg).
9. Schinzer, D.; Allagiannis, C.; Wichmann, S. *Tetrahedron* "Symposia in-Print" **1988**, 3851.
10. Schinzer, D.; Dettmer, G.; Ruppelt, M., Sólyom, S.; Steffen, J. *J.Org.Chem.* **1988**, 53, 3823.

11. All new compounds gave spectral and spectrometric data consistent with the assigned structures.

12. Typical procedure: To a solution of 460 mg (1.84 mmol) of compound **1** (X= C=O, R^1= H, R^2= Me) in 7 ml of toluene is added a trace of Amberlyst 15[8] at room temperature and the reaction mixture is stirred at room temperature for 6 h. The mixture is diluted with 30 ml of ether, filtered, and the solvent is removed under reduced pressure to obtain the crude product. The crude product is flash-chromatographed with 10% ethyl acetate/petroleum ether to obtain 300 mg (85%) of pure crystalline compound **2** (X= C=O, R^1= H, R^2= Me). Analytical and spectroscopic data of **2** (R_1= R_2= O, R_3= H, R_4= Me): mp.: 48 °C; IR (KBr): 3047, 2965, 2950, 2943, 2935, 2865, 2860, 2850, 1960, 1706, 1460, 1453, 1440, 1432, 1414, 1380, 1210, 850; ^{1}H-NMR ($CDCl_3$, 400 MHz): 1.21 (s, 3 H), 1.46 - 1.53 (m, 2 H), 1.57 (dd, 1 H, J= 6.8 Hz, J= 5.6 Hz), 1.77 (dtr, 1 H, J= 4.6 Hz, J= 13.4 Hz), 2.15 (ddtr, 1 H, J= 1.2 Hz, J= 9.7 Hz, J= 15.2 Hz), 2.31 (ddd, 1 H, J= 5.7 Hz, J= 12.9 Hz, J= 21.1 Hz), 2.38 - 2.46 (m, 4 H), 2.53 - 2.59 (m, 1 H), 4.66 (ddd , 1 H, J= 4.3 Hz, J= 5.7 Hz, J= 14.4 Hz), 4.74 (ddd, 1 H, J= 4.3 Hz, J= 5.3 Hz, J= 9.4 Hz); ^{13}C-NMR ($CDCl_3$, 100 MHz): 211.19, 202.65, 105.67, 78.31, 49.69, 40.21, 39.16, 38.01, 37.21, 32.90, 26.69, 24.09; MS (70 eV): m/z (%) = 176 (44), 161 (38), 148 (19), 119 (48), 105 (100), 91 (70), 84 (96); analysis calcd. for $C_{12}H_{16}O$: (176.26), Calcd. C: 81.77, H: 9.15, Found C: 81.64, H: 9.17.

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