Regio-, and Stereoselective Hydrohalogenation of Ynamides in Terminal Alkynes and 1,3- Diynes

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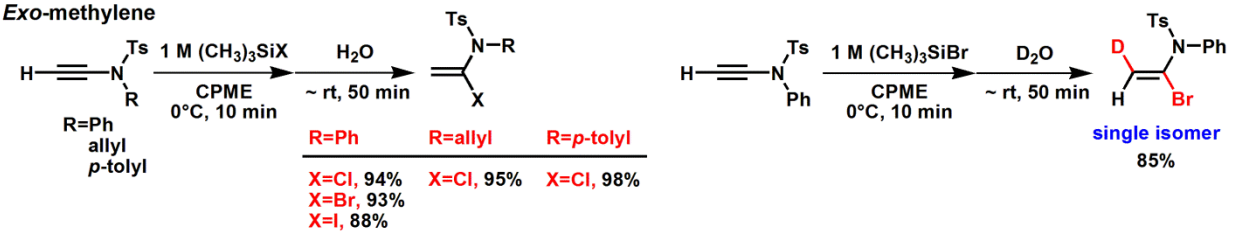
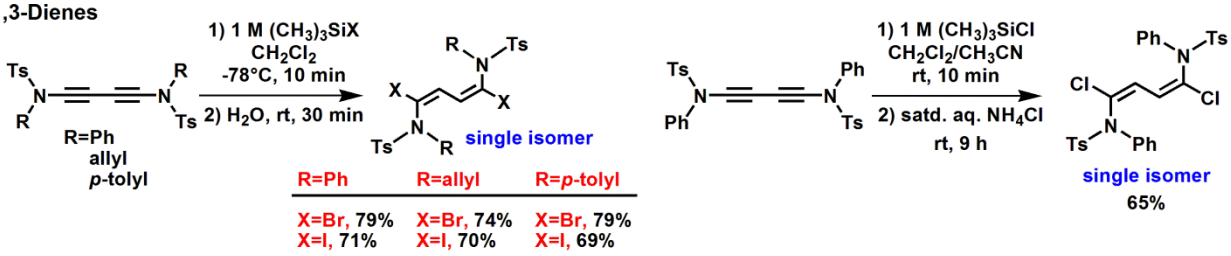
1. Summary

a) Ohashi, K.; Ide, M.; Mihara, S.; Sato, A. H.; Iwasawa, T. *Tetrahedron. Lett.* 2014, in press.

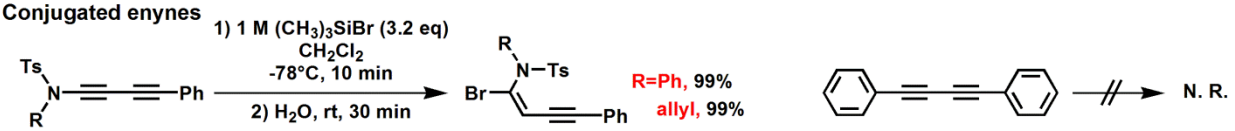
① *Exo*-methylene



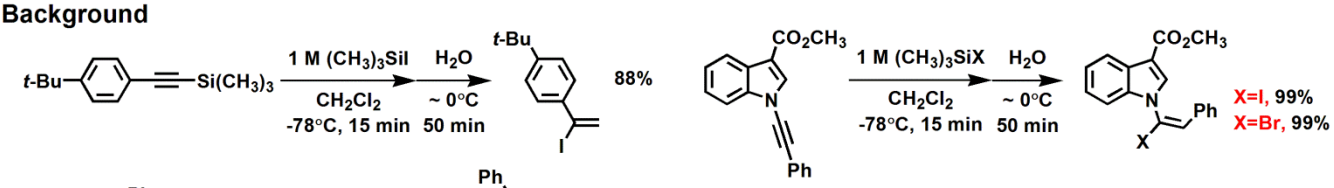
② 1,3-Dienes



③ Conjugated enynes

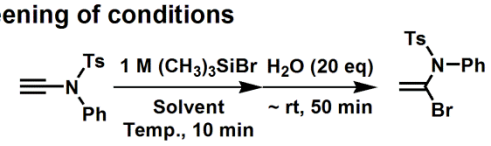


2. Background

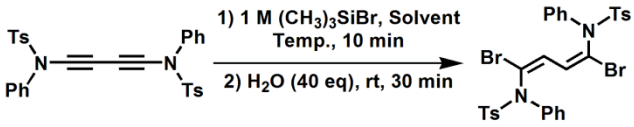


1. Sato, A.H.; Mihara, S.; Iwasawa, T. *Tetrahedron Lett.* 2012 *53*, 3585-3589.
2. Sato, A.H.; Ohashi, K.; Iwasawa, T. *Tetrahedron Lett.* 2013 *54*, 1309-1311.
3. Sato, A.H.; Ohashi, K.; Iwasawa, T. *Tetrahedron Lett.* 2013 *54*, 2878-2881.

3. Screening of conditions

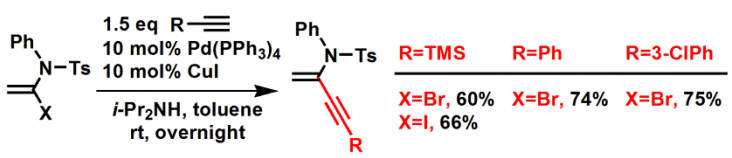


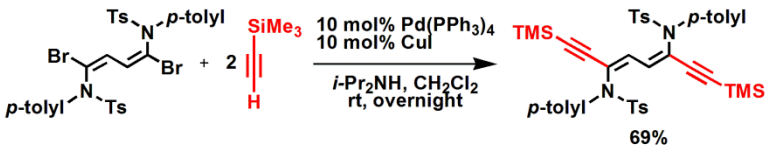
TMSBr (eq)	Solvent	Temp./°C	Yield/%
2.0	CH_2Cl_2	-78	56
1.2	CH_2Cl_2	-78	89
1.2	THF	-78	91
1.2	diethyl ether	-78	94
1.2	CPME	-78	95
1.2	CPME	0	93



TMSBr (eq)	Solvent	Temp./°C	Diyne/%	Diene/%
3.2	CH_2Cl_2	-78	0	79
3.2	CH_2Cl_2	0	2	68
1.2	CH_2Cl_2	0	28	44
2.4	CH_2Cl_2	0	12	60
3.2	Acetone	rt	4	60
3.2	Toluene	rt	28	52
3.2	THF	rt	72	24

4. Synthetic application





5.They are quite labile...