Synthesis of Allenes *via* Reduction of Acetylenic Tosylhydrazones

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Summary The reduction of tosylhydrazones of conjugated acetylenic ketones occurs with migration of one of the acetylenic bonds, providing a mild synthesis of allenes.

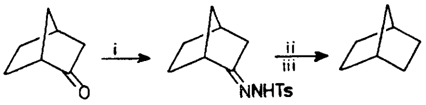
The reduction of tosylhydrazones by catecholborane (CB)[1] and other reagents[2] provides a mild alternative to the Wolff–Kishner and Clemmensen reductions [equation (1)].

TABLE. Formation of allenes *via* reduction of tosylhydrazones of conjugated acetylenic ketones.

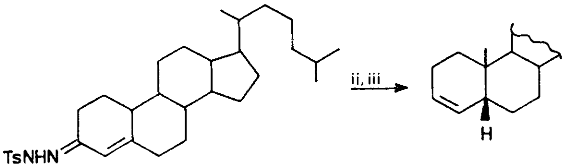
Ketone[a]	Product	Yield[b]/%	ν[c]/cm^{-1}	δ[d]
Oct-3-yn-2-one	Octa-2,3-diene	78 (64)	1950	1·02 (m,3H), 1·35—2·1 (m,9H), 4·80 (m,1H), 5·50 (m,1H)
But-1-yn-3-one	Buta-1,2-diene	49	1960	1·50 (m,3H), 4·45 (m,2H), 4·80 (m,1H)
4-Phenylbut-3-yn-2-one	1-Phenylbuta-1,2-diene	84 (75)	1960	1·60 (dd,3H), 5·5 (m,1H), 6·12 (m,1H), 7·3 (m,5H)
1-Phenylbut-2-yn-1-one	1-Phenylbuta-1,2-diene	30	1960	1·60 (dd,3H), 5·5 (m,1H), 6·12 (m,1H), 7·3 (m,5H)

[a] The ketones were first converted into the tosylhydrazone derivatives. [b] By n.m.r. analysis; yields in parentheses are those of isolated products. [c] Allene stretch region. [d] Solvent was $CDCl_3$.

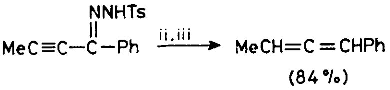
The reduction of tosylhydrazones of α,β-unsaturated carbonyl compounds is accompanied by the regiospecific migration of the double bond[3] [equation (2)].



(1)



(2)



$$\mathrm{MeC{\equiv}C{-}\overset{\overset{NNHTs}{\|}}{C}{-}Ph} \xrightarrow{\text{ii,iii}} \mathrm{MeCH{=}C{=}CHPh}$$

(84%)

(3)

i, H_2NNHTs; ii, CB; iii, $NaOAc{\cdot}3H_2O$. Ts = p-$MeC_6H_4SO_2$.

We have found that a regiospecific migration also occurs during the reduction of tosylhydrazones derived from conjugated acetylenic ketones to produce allenes in good yield [equation (3)].

The selectivity of catecholborane[4] and the mild reaction conditions (room temp.) make this synthesis a valuable addition to the existing routes to allenes.[5] The results are summarized in the Table.

The reduction of the tosylhydrazone of oct-3-yn-2-one is representative. The tosylhydrazone, m.p. 66–68 °C, was prepared in ethanol by mixing equimolar amounts of tosylhydrazide and the ketone; after 1 h at reflux, the product crystallized on cooling. The tosylhydrazone (5 mmol) was dissolved in $CHCl_3$ (5 ml) and CB (5 mmol) was added. The reduction was allowed to proceed at room temperature until complete (monitered by n.m.r. spectroscopy). Then, $NaOAc{\cdot}3H_2O$ (15 mmol) was added and the mixture was warmed for 1 h. The product (78% yield) was isolated by chromatography on silica gel.

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