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Regioselective Construction of Cyclohexene Derivatives by Diels–Alder Reactions of Nitro-olefins with Dienes and Subsequent Denitration with Tributyltin Hydride

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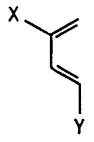
The nitro-group in the Diels–Alder adducts of nitro-olefins with dienes is replaced by hydrogen on treatment with tributyltin hydride, which offers a new method for the regioselective construction of cyclohexene derivatives.

We recently discovered a selective method for the denitration of nitroparaffins with tributyltin hydride,[1] but to date, the incorporation of this reaction into synthetic methodology has not been well established. Here we present a new method for the regioselective preparation of cyclohexene derivatives by Diels–Alder reactions of nitro-olefins with dienes and subsequent denitration with tributyltin hydride. In general it is rather difficult to construct cyclohexene derivatives regioselectively by the direct cycloaddition route.

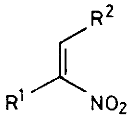
Nitro-olefins are well known to be excellent dienophiles in the Diels–Alder reaction; they require milder conditions than those required for simple olefins and the nitro-group controls the regiochemistry of the addition very effectively.[2,3] The nitro-group in the adduct is replaced by hydrogen with tributyltin hydride without interference from other functional groups. Results are shown in Table 1. Cycloaddition of 1-acetoxybuta-1,3-diene (**1**) or 1-methoxy-3-trimethylsilyloxybuta-1,3-diene (**2**)[2,4] with nitro-olefins (**3**)—(**5**) gave the respective regioselective adduct. Denitration of the adduct was carried out using the procedure of ref. 1. As methanol is readily eliminated from (**9**) or (**11**) on treatment with acid[4] or base,[5] 4,5-disubstituted cyclohex-2-enones can be prepared from them.

A nitro-group predominates over a carbonyl group in controlling the direction of the Diels–Alder reaction.[2,3] For example, cycloaddition of 3-nitrocyclohex-2-ene with penta-1,3-diene gave the adduct (**12**) in 83% yield as reported recently by Corey.[3] Denitration from this adduct with tributyltin hydride gave (**13**) in 86% yield, which was the reverse



(**1**) X = H, Y = OAc

(**2**) X = OSiMe$_3$, Y = OMe



(**3**) R^1 = Et, R^2 = H

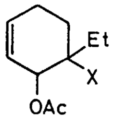
(**4**) R^1 = Me, R^2 = Et

(**5**) R^1 = Et, R^2 = Me

Table 1

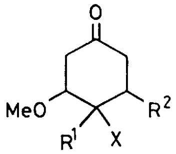
Diene	Nitro-olefin	Adduct (% yield)[a]	Reduction product (% yield)[a]
(**1**)	(**3**)	(**6**)[b] (40)	(**7**)[d] (85)
(**2**)	(**4**)	(**8**)[c] (71)	(**9**)[d] (82)
(**2**)	(**5**)	(**10**)[c] (63)	(**11**)[d] (81)

[a] Yields refer to pure isolated compounds. [b] Reflux in toluene for 12 h. [c] Reflux in benzene for 12 h followed by hydrolysis with 0·5 N-HCl. [d] Reflux in benzene for 1·5 h in the presence of Bu$_3$SnH (1·5 mol. equiv.) and azobis-isobutyronitrile (0·1 mol. equiv.).



(**6**) X = NO$_2$

(**7**) X = H

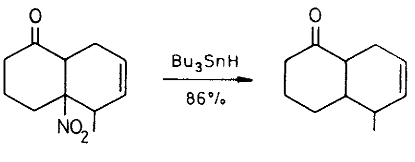


(**8**) R^1 = Me, R^2 = Et, X = NO$_2$

(**9**) R^1 = Me, R^2 = Et, X = H

(**10**) R^1 = Et, R^2 = Me, X = NO$_2$

(**11**) R^1 = Et, R^2 = Me, X = H



(**12**) (**13**)

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positional product of cycloaddition of cyclohex-2-enone with penta-1,3-diene.

The final products reported in the present paper are a mixture of stereoisomers but one regioisomer. Thus, the present method may find synthetic utility in the preparation of cyclohexene derivatives regioselectively.

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