

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

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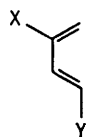
The nitro-group in the Diels–Alder adducts of nitro-olefins with dienes is replaced by hydrogen on treatment with tributyltin hydride, which offers a new method for the regioselective construction of cyclohexene derivatives.

We recently discovered a selective method for the denitration of nitroparaffins with tributyltin hydride,<sup>1</sup> 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

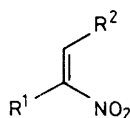
controls the regiochemistry of the addition very effectively.<sup>2,3</sup> The nitro-group in the adduct is replaced by hydrogen with tributyltin hydride without interference from other functional groups. Results are shown in Table 1. Cycloaddition of 1-acetoxybuta-1,3-diene (**1**) or 1-methoxy-3-trimethylsilyloxybuta-1,3-diene (**2**)<sup>2,4</sup> 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<sup>4</sup> or base,<sup>5</sup> 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.<sup>2,3</sup> 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.<sup>3</sup> Denitration from this adduct with tributyltin hydride gave (**13**) in 86% yield, which was the reverse



(1) X = H, Y = OAc

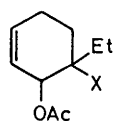
(2) X = OSiMe<sub>3</sub>, Y = OMe



(3) R<sup>1</sup> = Et, R<sup>2</sup> = H

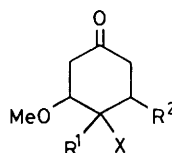
(4) R<sup>1</sup> = Me, R<sup>2</sup> = Et

(5) R<sup>1</sup> = Et, R<sup>2</sup> = Me



(6) X = NO<sub>2</sub>

(7) X = H



(8) R<sup>1</sup> = Me, R<sup>2</sup> = Et, X = NO<sub>2</sub>

(9) R<sup>1</sup> = Me, R<sup>2</sup> = Et, X = H

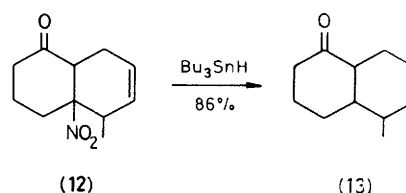
(10) R<sup>1</sup> = Et, R<sup>2</sup> = Me, X = NO<sub>2</sub>

(11) R<sup>1</sup> = Et, R<sup>2</sup> = Me, X = H

Table 1

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

<sup>a</sup> Yields refer to pure isolated compounds. <sup>b</sup> Reflux in toluene for 12 h. <sup>c</sup> Reflux in benzene for 12 h followed by hydrolysis with 0.5 N-HCl. <sup>d</sup> Reflux in benzene for 1.5 h in the presence of Bu<sub>3</sub>SnH (1.5 mol. equiv.) and azobis-isobutyronitrile (0.1 mol. equiv.).



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.

The present work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture.

*Received, 21st August 1981; Com. 1024*

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