Regioselective Diels–Alder Reactions. The Nitro Group as a Regiochemical Control Element [1]

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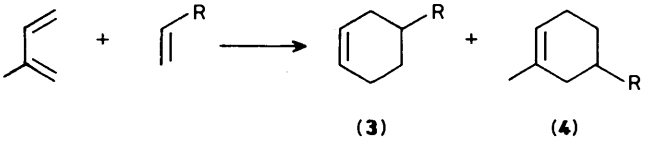
The sequence of the Diels–Alder reaction of α-nitroalkenes with dienes and subsequent denitration with Bu_3SnH provides a new method for the regioselective construction of cyclohexene derivatives.

Although the Diels–Alder reaction has been extensively used for the preparation of cyclic compounds, regiochemical control of the reaction is still the biggest unsolved problem. Regiochemistry is controlled to some extent when dienes or dienophiles are substituted with hetero-atoms, however, it is very difficult to control the direction of the addition of simple dienes to simple dienophiles. For example, the reaction of isoprene with alk-1-enes gives a mixture of regioisomers (**3**) and (**4**) as shown in Scheme 1. There are no good, direct methods leading to compounds (**3**) or (**4**) regioselectivity.



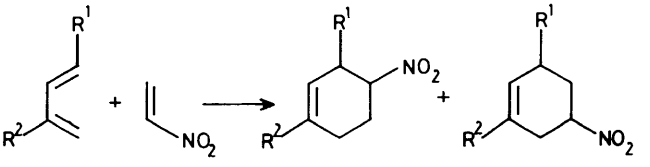
Scheme 1.

Here we report a simple solution to this problem. A new method is outlined in Scheme 5, in which the nitro group is used as an effective regiochemical control element.[2] Both regioisomers of the nitroalkene are readily available,[3] and both isomers of the cyclohexene product can be prepared by this method. Although other electron-withdrawing groups such as CN, CO_2R, or SO_2R are good candidates as regiochemical control elements in the Diels–Alder reaction, the nitro group has proved to be the best. The nitro group controls the direction of addition more effectively than other groups,[2] and is selectively removed without interference from other functional groups.[1] Recently, vinyl sulphones have been demonstrated as useful alkene-equivalents in the Diels–Alder reaction,[4] where the cycloaddition of phenyl vinyl sulphone, alkylation with alkyl halides, and desulphonylation are involved. This sequence is an excellent method of preparing one regioisomer such as (**3**) in Scheme 5. However, compound (**4**) cannot be prepared by this method, for 1-sulphonylalk-1-enes are not so reactive to dienes such as isoprene, and the regiochemistry is not easily controlled. In contrast, nitroalkenes are very reactive and both isomers react with isoprene to give compounds (**1**) and (**2**) in Scheme 5, respectively.

Results and Discussion

Nitroalkenes are well known to be excellent dienophiles in the Diels–Alder reaction, where the nitro group accelerates the reaction and the direction of the addition very effectively.[2] Although such reactions have been extensively used in organic synthesis,[2] nitroalkenes have never been used as alkene equivalents, because efficient methods for removing the nitro group have not been available until recent years. Recently, we have found that aliphatic nitro groups are readily removed by Bu_3SnH in the presence of azoisobutyronitrile (AIBN).[5] As this reaction proceeds with high functional selectivity, it is now considered as a useful synthetic reaction.[5] Combination of the Diels–Alder reaction of nitroalkenes with denitration provides a new method for the construction of 6-membered cyclic compounds as shown in Scheme 5.

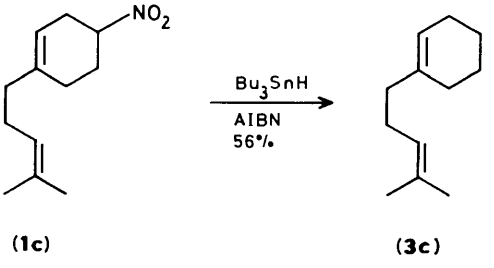
The regiochemistry of the addition of nitroethylene was first examined. It is well known that nitroethylene is extremely reactive toward various dienes.[3] In fact, nitroethylene reacted with (*E*)-penta-1,3-diene, isoprene, or myrcene at room temperature to give one regioisomer selectively. When the reaction was carried out at higher temperature, the selectivity was poor. The results are summarized in Table 1.



a; R^1 = Me, R^2 = H
b; R = H, R^2 = Me
c; R^1 = H, R^2 = $Me_2C{=}CHCH_2CH_2$

Scheme 2.

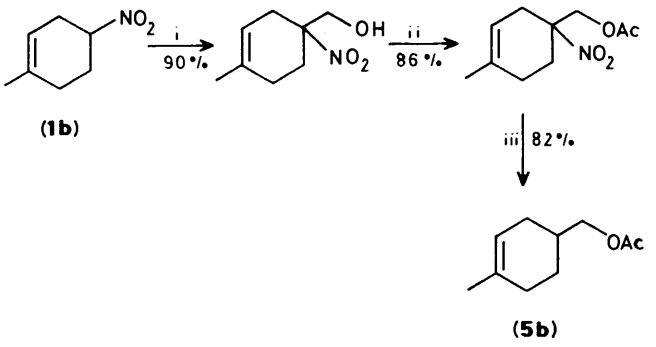
The nitro group present in the adducts can be removed with Bu_3SnH, however, denitration of compounds containing secondary nitro groups is more difficult than those containing tertiary ones.[6] For example, compound (**1c**) was converted into compound (**3c**) in 56% yield by heating a mixture of compound



Scheme 3.

(**1c**), Bu_3SnH (5 equiv.), and AIBN (0.5 equiv.) in toluene at 110 °C for 30 min. Compound (**3c**) can be regarded as addition product of myrcene with ethylene. However, it is very difficult to obtain compound (**3c**) by the direct route, which requires high temperature and high pressure.[7]

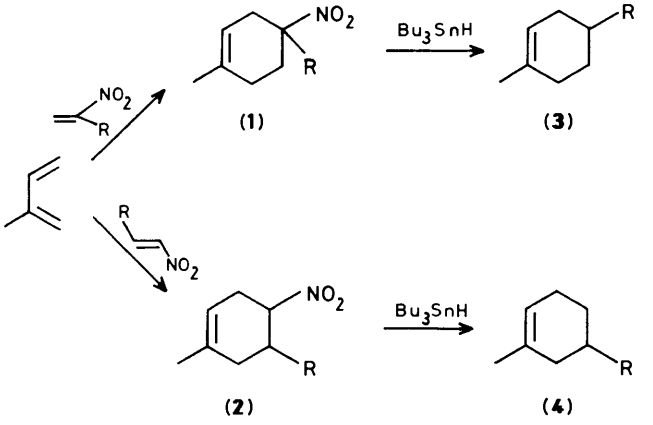
The nitro group can be removed after alkylation of the Diels–Alder adducts. For example, compound (**1b**) was converted into the acetoxymethylated compound (**5b**) as shown in Scheme 4.



Scheme 4. *Reagents:* i, 35%-HCHO–NaOH (0.1 equiv.)–Pr^iOH; ii, AC_2O–pyridine; iii, Bu_3SnH (1.2 equiv.)–AIBN (0.2 equiv.)–benzene, 80 °C, 2 h

Hydroxymethylation of (**1b**) was simply carried out by stirring a mixture of (**1b**), 35%-HCHO, and a catalytic amount of NaOH in isopropyl alcohol at room temperature. Subsequent acetylation and denitration gave compound (**5b**) in good yield, where denitration was carried out by heating a mixture of nitro compound, Bu_3SnH (1.2 equiv.), and AIBN (0.2 equiv.) in benzene at 80 °C for 2 h.

The present method can be extended to a general synthesis of cyclohexenes as shown in Scheme 5. For example, isoprene

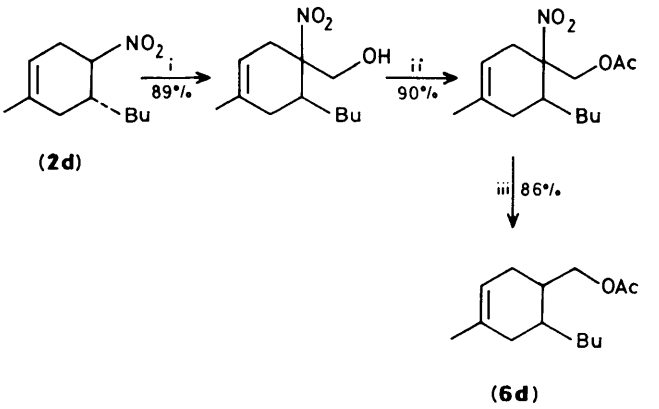


Scheme 5.

reacts with 2-nitrohex-1-ene or 1-nitrohex-1-ene to give the corresponding adduct, (**1d**) or (**2d**) respectively. Subsequent denitration gives compounds (**3d**) and (**4d**), respectively. The results are summarized in Table 2. As both regio-isomers of nitroalkenes are readily available, both regio-isomers of the [2 + 4] addition product of 1-alkenes with dienes are readily prepared independently by this method. High regioselectivity is due to the strong activating power of the nitro group.

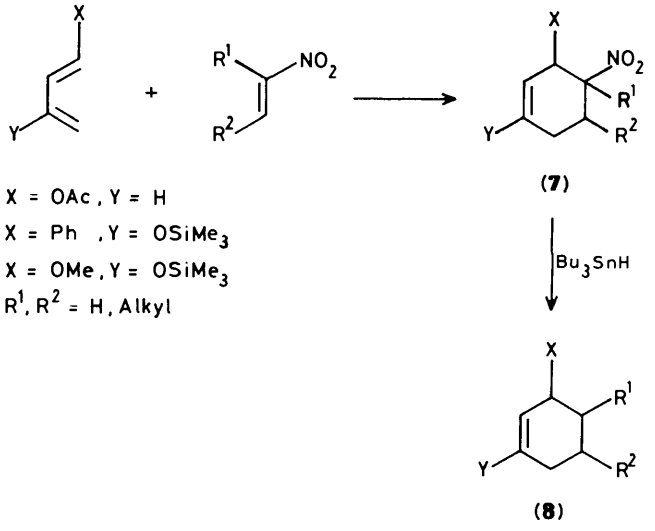
The transformations illustrated in Scheme 4 can be applied to compound (**2d**) which is converted into compound (**6d**) as shown in Scheme 6. The sequence given in Schemes 4 and 6 can be regarded as the cycloaddition of allyl acetates to dienes. Compounds (**5b**) and (**6d**) could not be prepared by the direct Diels–Alder reaction of isoprene with allyl acetates, since this reaction gives the mixture of regioisomers.

The Diels–Alder reaction of hetero-substituted 1,3-dienes with nitroalkenes and subsequent denitration provides a new method for the preparation of functionalized ring compounds and various hetero substituted 1,3-dienes are now available.[8] 1-Acetoxybuta-1,3-diene, and 3-trimethylsilyloxybuta-1,3-diene were selected as typical dienes. In general, such hetero-



Scheme 6. *Reagents:* 1, 35%-HCHO (0.1 equiv.)–Pr^iOH; ii, Ac_2O–pyridine; iii, Bu_3SnH (1.2 equiv.)–AIBN (0.2 equiv.), 80 °C, 2 h

substituted 1,3-dienes are more reactive than simple dienes, and the control of regiochemistry is much easier than with simple dienes. The general sequence is shown in Scheme 7 and the results are summarized in Table 3.



Scheme 7.

These reactions were completely regioselective to give compounds (**7a**—**h**), respectively, in which the nitro and oxygen functions are orientated at the *ortho*- or *para*-positions, which is in accord with MO predictions.[9] This trend is well understood in most Diels–Alder reactions, however the stereochemistry of these reactions is rather complicated. It is well known that the *endo*-adducts are formed preferentially in the Diels–Alder reactions.[2,9] This rule can be applied to the present case also, but the stereocontrol is not always perfect. The reaction of 1-acetoxybuta-1,3-diene with 2-nitroalk-1-enes gives compounds (**7a**) or (**7c**), respectively, where R is Et or $PhCH_2$. Compounds (**7a**) and (**7c**) are isolated as a mixture of two stereo-isomers of ratio *ca.* 80:20 as determined by g.l.c. The major product is probably the *endo*-nitro adduct. As denitration with Bu_3SnH proceeds *via* free radical intermediates, the stereospecificity is lost during denitration. So the stereochemistry of the addition is not retained after denitration to give the thermodynamically controlled product. However, the addition of 1-nitroalk-1-enes with 1-acetoxybuta-1,3-diene proceeds stereoselectively to give compounds (**7b**) or (**7d**), respectively, where R is Et or Pr^i. As the

Table 1. Diels–Alder reaction of nitroethylene

R^1	R^2	Conditions	Product (1)	Yield (%)	A:B[a]
Me	H	Benzene, r.t., 9 h	(**1a**)	79	100:0
H	Me	Benzene, 80 °C, 5 h	(**1b**)	86	95:5
H	Me	$CHCl_3$, r.t., 36 h	(**1b**)	83	100:0
H	$CH_2CH_2CH{=}CMe_2$	Benzene, 80 °C, 8 h	(**1c**)	71	78:22
H	$CH_2CH_2CH{=}CMe_2$	$CHCl_3$, r.t., 36 h	(**1c**)	66	95:5

[a] The ratio of regioisomers was determined by g.l.c. and n.m.r. spectroscopy.

Table 2. Diels–Alder reaction of nitroalkene and subsequent denitration (Scheme 2)

R	Product (1) or (2)[a]	Yield (%)	Denitration[b]	Product	Yield (%)
Bu	(**1d**)	72	A	(**3d**)	80
Bu	(**2d**)	70	B	(**4d**)	52
$PhCH_2$	(**1e**)	61	A	(**3e**)	85
$PhCH_2$	(**2e**)	65	B	(**4e**)	50

[a] The reaction was carried out in $CHCl_3$ at reflux for 72 h. Regioselectivity was more than 95%. [b] A; Bu_3SnH (1.2 equiv.), AIBN (0.2 equiv.), benzene, 80 °C, 2 h. B: Bu_3SnH (5 equiv.), AIBN (0.5 equiv.), toluene, 110 °C, 0.5 h.

Table 3. Diels–Alder reaction of hetero-substituted dienes with nitroalkenes and subsequent denitration

X	Y	R^1	R^2	Conditions	Adducts	Yield (%)	Denitration[a]	Product	Yield (%)
OAc	H	Et	H	Toluene, 110 °C, 10 h	(**7a**)	50	A	(**8a**)	67
OAc	H	H	Et	Toluene, 110 °C, 10 h	(**7b**)	45	B	(**8b**)	45
OAc	H	$PhCH_2$	H	Toluene, 110 °C, 12 h	(**7c**)	56	A	(**8c**)	78
OAc	H	H	Me_2CH	Toluene, 110 °C, 72 h	(**7d**)	63	B	(**8d**)	45
Ph	$OSiMe_3$	Et	H	Toluene, 110 °C, 4 h	(**7e**)	86	A	(**8e**)	84
Ph	$OSiMe_3$	H	Et	Toluene, 110 °C, 2 h	(**7f**)	90	B	(**8f**)	59
OMe	$OSiMe_3$	Et	Me	Benzene, 80 °C, 10 h	(**7g**)	71	A	(**8g**)	82
OMe	$OSiMe_3$	Me	Et	Benzene, 80 °C, 16 h	(**7h**)	63	A	(**8h**)	81

[a] Conditions as in Table 2.

Table 4. Stereochemistry of the cycloaddition of hetero-substituted dienes and denitration

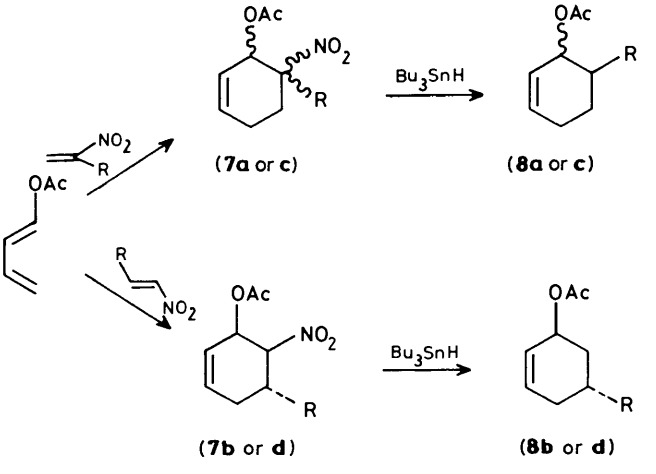
Compound (7)	*endo*:*exo*[a]	Compound (8)	*trans*:*cis*[b]
(**7a**)	80:20	(**8a**)	75:25
(**7b**)	100:0	(**8b**)	100:0
(**7c**)	85:15	(**8c**)	77:23
(**7d**)	100:0	(**8d**)	100:0
(**7e**)	66:34	(**8e**)	65:35
(**7f**)	100:0	(**8f**)	100:0
(**7g**)	77:23	(**8g**)	Complex mixtures
(**7h**)	75:25	(**8h**)	Complex mixtures

[a] With respect to the nitro group. The ratio was determined by g.l.c. and n.m.r. spectroscopy. [b] The ratio was determined by g.l.c. and n.m.r. spectroscopy.

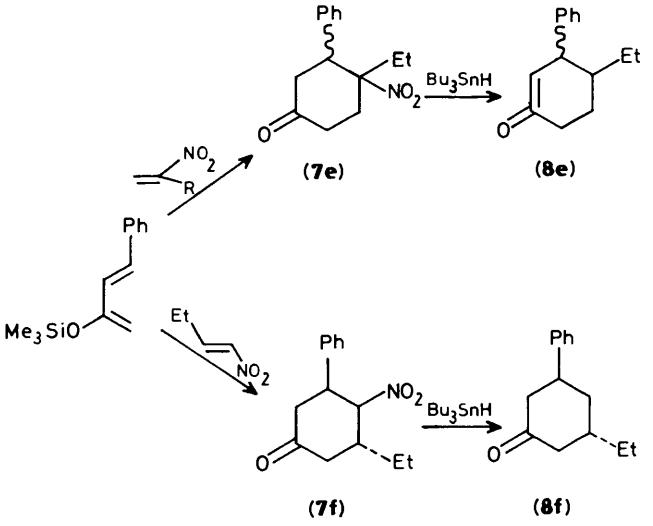
nitro groups are secondary in these compounds, subsequent denitration leads to compounds (**8b**) or (**8d**) stereoselectively as shown in Scheme 8 and Table 4.

When 3-trimethylsilyloxybuta-1,3-dienes were used, cyclohexanones were obtained regioselectively. For example, 1-phenyl-3-trimethylsilyloxybuta-1,3-diene reacted with 2-nitrobut-1-ene or 1-nitrobut-1-ene to give the adduct (**7e**) or (**7f**), respectively, with complete regioselectivity. Compound (**7e**) was a mixture of two stereoisomers, ratio of 65:35, but compound (**7f**) was a single isomer. Subsequent denitration then gave compounds (**8e**) and (**8f**) as shown in Scheme 9.

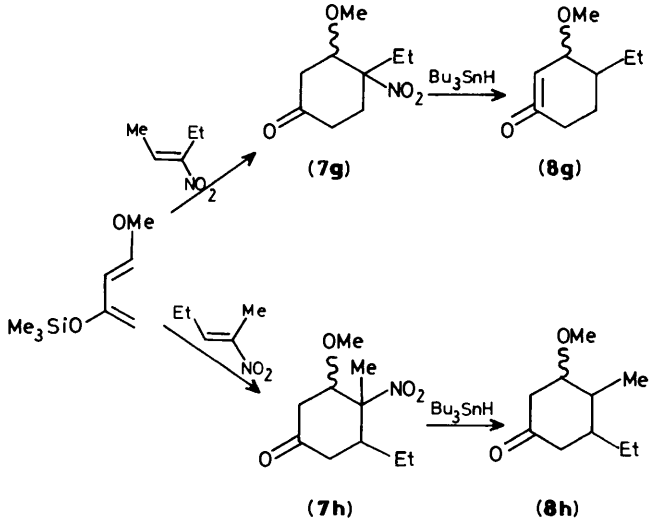
When 1-methoxy-3-trimethylsilyloxybuta-1,3-diene[10] was used, the sequence of the Diels–Alder reaction with nitroalkenes followed by denitration gave methoxy-substituted cyclohexanones, which were readily converted into cyclohexenones by elimination of methanol.[11] In these cases, it was very difficult to control the stereochemistry of the addition and denitration, but the regiochemistry was perfectly controlled (Scheme 10).



Scheme 8.

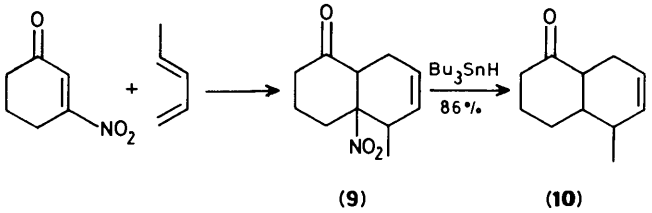


Scheme 9.



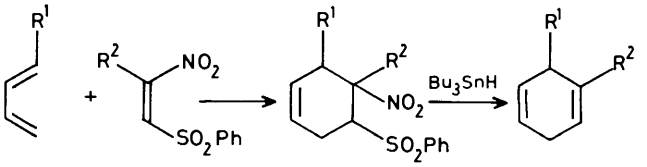
Scheme 10.

A nitro group is better at controlling the direction of the Diels–Alder reaction than other electron withdrawing groups such as carbonyl, cyano, or sulphonyl.[2,12] For example, the cycloaddition of 3-nitrocyclohex-2-en-1-one with (*E*)-penta-1,3-dienes give the adduct (**9**) in 83% yield as reported recently by Corey.[12] Denitration from this adduct with Bu_3SnH gives compound (**10**) in 86% yield; the opposite regiochemistry is observed in the reaction between cyclohex-2-en-1-one and (*E*)-penta-1,3-diene (Scheme 11).



Scheme 11.

We have recently reported the Diels–Alder reaction of β-sulphonyl nitroalkenes with dienes, where the nitro group



Scheme 12.

controls the direction of addition more effectively than the sulphonyl group.[13] Subsequent treatment of the adduct with Bu_3SnH results in the clean elimination of both the sulphonyl and the nitro group to give cyclic 1,4-dienes.[13] β-Sulphonyl nitroalkenes can be regarded as a regio-controlled equivalent of alkynes with regard to the Diels–Alder reaction. Details of this reaction will be reported in a separate paper.

Thus, the sequence of the Diels–Alder reaction involving nitroalkenes and subsequent denitration with Bu_3SnH provides a very useful synthetic method. As each regioisomer of a particular nitroalkene is readily prepared, the corresponding Diels–Alder cycloadducts are available with high regioselectivity.

Experimental

Nitroethylene was prepared by dehydration of nitroethanol with phthalic anhydride.[14] Other nitroalkenes were prepared by elimination of acetic acid from β-acetoxy nitro compounds with sodium acetate.[3] Hetero-substituted 1,3-dienes were prepared according to literature procedures.[8]

Diels–Alder Reaction of Nitroethylene with Isoprene.—A solution of isoprene (5.78 g, 85 mmol), nitroethylene (1.24 g, 17 mmol), and 4-methyl-2,6-di-t-butylphenol (BHT, 0.12 g, 0.85 mmol) in benzene (10 ml) was refluxed for 5 h. The reaction mixture was then passed through a short column (silica gel; benzene–hexane) and the crude product was further purified by distillation, b.p. 47–48 °C/0.8 mmHg, to give compound (**1b**), (2.0 g, 86%), $\nu_{max.}$(neat) 1 350, 1 540, and 1 650 cm^{-1}; δ(100 MHz; $CDCl_3$) 1.68 (s, 3 H, Me), 1.98—2.70 [m, 6 H, $(CH_2)_3$], 4.48 (m, 1 H, $CHNO_2$), and 5.34 (m, 1 H, CH=C) (Found: C, 59.35; H, 7.8; N, 10.0. $C_7H_{11}NO_2$ requires C, 59.55; H, 7.86; N, 9.92).

The same reaction was carried out in $CHCl_3$ and worked up in the same way. The isomer ratio was determined by g.l.c. with a 2 m column packed with silicon DC-550. Other Diels–Alder reactions of nitroethylene were carried out in the same way and the following compounds were prepared.

3-*Methyl*-4-*nitrocyclohexene* (**1a**). B.p. 52 °C/1 mmHg (lit.,[15] 93 °C/8 mmHg), $\nu_{max.}$(neat) 1 350, 1 540, and 1 650 cm^{-1}; δ(100 MHz; $CDCl_3$) 0.92 (d, *J* 8 Hz, Me), 1.06 (d, *J* 8 Hz, Me), 1.96—2.36 (m, 4 H, CH_2CH_2), 2.68—3.04 (m, 1 H, CH), 4.45 (m, 1 H, $CHNO_2$), and 5.34—5.53 (m, 2 H, CH=CH). G.l.c. analyses showed that compound (**1a**) consisted of two stereoisomers, ratio 68:32.

1-(4-*Methylpent*-3-*enyl*)-4-*nitrocyclohexene* (**1c**). B.p. 116–118 °C/1 mmHg, $\nu_{max.}$(neat) 1 350, 1 540, and 1 670 cm^{-1}; δ(100 MHz; $CDCl_3$) 1.56 (s, 3 H, Me), 1.64 (s, 3 H, Me), 1.82—2.68 [m, 10 H, $(CH_2)_5$], 4.28—4.54 (m, 1 H, $CHNO_2$), 4.82—5.04 (m, 1 H, CH=C), and 5.18—5.38 (m, 1 H, CH=C) (Found: C, 68.7; H, 9.2; N, 7.05. $C_{12}H_{19}NO_2$ requires C, 68.83; H, 9.15; N, 6.69%).

Diels–Alder Reaction of Isoprene with Nitroalkenes.—4-*Butyl*-1-*methyl*-4-*nitrocyclohexene* (**1d**). A solution of isoprene (3.40 g, 50 mmol), 2-nitrohex-1-ene (1.39 g, 10 mmol), and BHT (0.11 g, 0.5 mmol) in $CHCl_3$ (5 ml) was refluxed for 72 h. The reaction mixture was subjected to column chromatography (silica gel; benzene–hexane) followed by distillation to give compound (**1d**)

(1.48 g, 72%), b.p. 65 °C/1 mmHg, $\nu_{max.}$ 1 350, 1 540, and 1 660 cm^{-1}; δ (100 MHz; $CDCl_3$) 0.90 (t, 3 H, *J* 8 Hz, Me), 1.0—1.4 (m, 4 H, CH_2CH_2), 1.65 (s, 3 H, Me), 1.5—2.8 [m, 8 H, $(CH_2)_4$], and 5.12—5.28 (m, 1 H, CH=C). The following compounds were prepared by this procedure. Elemental analyses were performed after denitration and g.l.c. analysis revealed high levels of isomeric purity.

5-*Butyl*-1-*methyl*-4-*nitrocyclohexene* (**2d**). B.p. 65 °C/1 mmHg $\nu_{max.}$(neat) 1 350, 1 540, and 1 670 cm^{-1}; δ (100 MHz; $CDCl_3$) 0.85 (t, 3 H, *J* 8 Hz, Me), 1.0—1.6 [m, 6 H, $(CH_2)_3$], 1.65 (s, 3 H, Me), 1.5—2.8 (m, 5 H, CH_2CH_2CH), 4.20—4.52 (m, 1 H, $CHNO_2$), and 5.16—5.22 (m, 1 H, CH=C).

4-*Benzyl*-1-*methyl*-4-*nitrocyclohexene* (**1e**). b.p. 135—136 °C/0.6 mmHg, $\nu_{max.}$ 1 350, 1 530, and 1 670 cm^{-1}; δ (100 MHz; $CDCl_3$) 1.62 (s, 3 H, Me), 1.70—2.88 [m, 6 H, $(CH_2)_3$], 3.06 (s, 2 H, PhCH_2), 5.10—5.32 (m, 1 H, CH=C), and 7.0—7.4 (m, 5 H, ArH).

5-*Benzyl*-1-*methyl*-4-*nitrocyclohexene* (**2e**). B.p. 135—137 °C/1 mmHg, $\nu_{max.}$ 1 350, 1 530, and 1 670 cm^{-1}; δ (100 MHz; $CDCl_3$) 1.64 (s, 3 H, Me), 1.65—2.78 (m, 5 H, CH_2CH_2CH), 2.80 (d, 2 H, *J* 8 Hz, $PhCH_2$), 4.25—4.55 (m, 1 H, $CHNO_2$), 5.10—5.35 (m, 1 H, CH=C), and 7.0—7.4 (m, 5 H, Ar).

Diels–Alder Reaction of 1-*Acetoxybuta*-1,3-*diene*.—3-*Acetoxy*-4-*ethyl*-4-*nitrocyclohexene* (**7a**). A solution of 1-acetoxybuta-1,3-diene (3.88 g, 34.6 mmol), 2-nitrobut-1-ene (1.75 g, 17.3 mmol), and BHT (0.19 g, 0.87 mmol) in toluene (3 ml) was refluxed for 10 h. The reaction mixture was subjected to column chromatography (silica gel; benzene–hexane) to give compound (**7a**) (1.83 g, 50%). G.l.c. analyses showed that compound (**7a**) consisted of two isomers, ratio *ca.* 80:20, $\nu_{max.}$ 1 350, 1 540, and 1 750 cm^{-1}; δ (100 MHz; $CDCl_3$) 0.86 (t, 3 H, *J* 8 Hz, Me), 1.92 and 2.04 (each s, 3 H, Ac), 1.6—2.5 (m, 6 H, CH_2 and CH_2CH_2), 5.22 (m, 1 H, C*H*OAc), 5.64—5.96 (m, 2 H, CH=CH). The isomer ratio was confirmed by integration of the two singlets at δ 1.92 and 2.04. The following compounds were prepared by this procedure. Elemental analysis were performed after denitration.

3-*Acetoxy*-5-*ethyl*-4-*nitrocyclohexene* (**7b**). $\nu_{max.}$ 1 350, 1 540, and 1 730 cm^{-1}; δ (100 MHz; $CDCl_3$) 0.96 (t, 3 H, Me), 1.5—2.7 (m, 5 H, CH_2CHCH_2), 2.04 (s, 3 H, Ac), 4.50—4.68 (m, 1 H, $CHNO_2$), 5.3—5.4 (m, 1 H, C*H*OAc), and 5.60—6.10 (m, 2 H, CH=CH). N.m.r. analysis showed that compound (**7b**) was one isomer.

3-*Acetoxy*-4-*benzyl*-4-*nitrocyclohexene* (**7c**). $\nu_{max.}$ 1 350, 1 540, 1 648, and 1 730 cm^{-1}; δ (100 MHz; $CDCl_3$) 1.94 and 2.16 (s, 3 H, Me), 2.08—2.54 (m, 4 H, CH_2CH_2), 2.84—3.46 (m, 2 H, CH_2Ph), 5.46—5.66 (m, 1 H, C*H*OAc), 5.76—6.06 (m, 2 H, CH=CH), and 7.0—7.4 (m, 5 H, ArH).

3-*Acetoxy*-5-*isopropyl*-4-*nitrocyclohexene* (**7d**). $\nu_{max.}$ 1 350, 1 535, and 1 730 cm^{-1}, δ (100 MHz; $CDCl_3$) 0.84 (d, 3 H, *J* 8 Hz, Me), 1.00 (d, 3 H, *J* 8 Hz, Me), 2.00 (s, 3 H, Ac), 1.6—2.6 (m, 4 H, CH, $CHCH_2$), 4.60 (m, 1 H, $CHNO_2$), 5.4—5.6 (m, 1 H, C*H*OAc), 5.6—6.0 (m, 2 H, CH=CH). These data indicate that compound (**7d**) is present as a single isomer.

Diels–Alder Reaction of 3-*Silyloxybuta*-1,3-*diene*.—4-*Ethyl*-4-*nitro*-3-*phenylcyclohexanone* (**7e**). A solution of 1-phenyl-3-trimethylsilyloxybuta-1,3-diene (6.54 g, 30 mmol), 2-nitrobut-1-ene (1.52 g, 10 mmol), and BHT (0.17 g, 0.75 mmol) in toluene (10 ml) was refluxed for 4 h. A solution of 2M HCl (2 ml) was added to the resulting mixture and stirring was continued for 60 min. The usual work-up (extraction with ether, washing with water, drying with $MgSO_4$, and concentration) followed by column chromatography (silica gel; benzene–hexane) gave compound (**7e**) (3.3 g, 86%), $\nu_{max.}$ 1 350, 1 530, and 1 710 cm^{-1}; δ (100 MHz; $CDCl_3$) 0.66—0.98 (m, 3 H, Me), 1.10—1.56 (m, 2 H, CH_2), 1.67—2.02 (m, 2 H, CH_2), 2.04—2.82 (m, 4 H, CH_2COCH_2), 3.16—3.42 (m, 1 H, PhC*H*), and 6.8—7.4 (m, 5 H, ArH).

5-*Ethyl*-4-*nitro*-3-*phenylcyclohexanone* (**7f**). The same procedure using 1-nitrobut-1-ene gave compound (**7f**). $\nu_{max.}$ 1 350, 1 530, and 1 700 cm^{-1}; δ (100 MHz; $CDCl_3$) 0.92 (t, 3 H, *J* 8 Hz, Me), 1.2—1.7 (m, 3 H, CH_2CH), 2.05—2.89 (m, 4 H, CH_2COCH_2), 3.2—3.6 (m, 1 H, CHPh), 4.7—5.0 (m, 1 H, $CHNO_2$), and 7.1—7.4 (m, 5 H, Ar). G.l.c. and n.m.r. analysis showed that compound (**7e**) was a mixture of two stereoisomers and compound (**7f**) was one isomer. Elemental analyses were performed after denitration.

4-*Ethyl*-3-*methoxy*-5-*methyl*-4-*nitrocyclohexanone* (**7g**). A solution of 1-methoxy-3-trimethylsilyloxybuta-1,3-diene (2.58 g, 15 mmol) and 3-nitropent-2-ene (1.15 g, 10 mmol) in benzene (10 ml) was refluxed for 10 h. The benzene was removed and tetrahydrofuran (10 ml) and 0.5M-HCl (1 ml) was added and the resulting mixture was stirred at 0 °C for 30 min. The usual work-up followed by distillation gave compound (**7g**) (1.52 g, 71%), b.p. 112—114 °C/0.6 mmHg, $\nu_{max.}$ 1 350, 1 540, and 1 720 cm^{-1}; δ (100 MHz; $CDCl_3$) 0.9—1.3 (m, 6 H, Me), 1.9—3.0 (m, 7 H, CH_2, $CHCH_2COCH_2$), 3.36 (s, 3 H, OMe), 4.32 (t, 1 H, *J* 8 Hz, C*H*OMe). Compound (**7g**) was analysed by g.l.c. as a mixture of two stereoisomers, ratio 77:23.

5-*Ethyl*-3-*methoxy*-4-*methyl*-4-*nitrocyclohexanone* (**7h**). The same procedure using 2-nitropent-2-ene gave compound (**7h**), $\nu_{max.}$ 1 350, 1 540, and 1 720 cm^{-1}; δ (100 MHz; $CDCl_3$) 0.88 (t, 3 H, *J* 8 Hz, Me), 1.1—1.3 (m, 2 H, CH_2), 1.64 (s, 3 H, Me), 1.9—3.0 (m, 5 H, $CHCH_2COCH_2$), 3.88 (s, 3 H, OMe), 4.00—4.24 (m, 1 H, C*H*OMe). Compound (**7h**) was analysed by g.l.c. and found to be a mixture of two stereoisomers, ratio 75:25.

Introduction of Electrophiles to the Diels–Alder Adducts.—4-*Acetoxymethyl*-1-*methyl*-4-*nitrocyclohexene*. A solution of compound (**1d**) (1.27 g, 9 mmol), HCHO (35%; 0.88 g, 11 mmol), and NaOH (0.05 g) in propan-2-ol (10 ml) was stirred at room temperature for 1 h. To this was added 2M-HCl (5 ml) and the reaction mixture was extracted with ether. The usual work-up followed by distillation gave the hydroxymethylated compound, (1.40 g, 90%), which was acetylated by stirring a mixture of the hydroxymethylated nitro compound (1.31 g, 7.7 mmol) and acetic anhydride (0.98 g, 9.2 mmol) in pyridine (1.5 ml) at room temperature for 1 h, then treating the mixture with 2 M-HCl (15 ml) prior to extraction with ether. The usual work-up followed by distillation gave 4-acetoxymethyl-1-methyl-4-nitrocyclohexene, (1.40 g, 86%), $\nu_{max.}$ 1 350, 1 540, 1 670, and 1 745 cm^{-1}; δ (100 MHz; $CDCl_3$) 1.66 (s, 3 H, Me), 1.8—2.8 (m, 6 H, CH_2CH_2, CH_2), 2.08 (s, 3 H, Ac), 4.40 (s, 2 H, CH_2O), and 5.12—5.40 (m, 1 H, CH=C).

4-*Acetoxymethyl*-5-*butyl*-1-*methyl*-4-*nitrocyclohexene*. This compound was prepared by the same procedure as that described above: $\nu_{max.}$ 1 350, 1 540, 1 670, and 1 750 cm^{-1}; δ (100 MHz; $CDCl_3$) 0.87 (t, 3 H, *J* 8 Hz, Me), 1.0—1.7 [m, 6 H, $(CH_2)_3$], 1.65 (s, 3 H, Me), 1.7—2.8 (m, 5 H, CH_2CH_2CH), 2.06 (s, 3 H, Ac), 4.24 (s, 2 H, CH_2O), and 5.16—5.34 (m, 1 H). Elemental analysis of these compounds were performed after denitration.

Typical Procedure for the Denitration of Secondary Nitro Compounds.—3-*Acetoxy*-5-*ethylcyclohexene* (**8b**). A mixture of compound (**7b**) (0.85 g, 4 mmol), Bu_3SnH (5.82 g, 20 mmol), and AIBN (0.32 g, 2 mmol) in toluene (5 ml) was heated at 110 °C for 30 min before being subjected to column chromatography (silica gel; benzene–hexane) to give compound (**8b**) (0.87 g, 45%), which was analysed by g.l.c. and n.m.r. spectroscopy to be one regio- and stereo-isomer, $\nu_{max.}$ 1 715 cm^{-1}; δ (100 MHz; $CDCl_3$) 0.92 (t, 3 H, *J* 8 Hz, Me), 1.18—2.34 [m, 7 H, $CH_2CH(CH_2)_2$], 2.04 (s, 3 H, Ac), 5.16—5.30 (m, 1 H, C*H*OAc),

5.58—6.08 (m, 2 H, CH=CH) (Found: C, 71.25; H, 9.50. $C_{10}H_{16}O_2$ requires C, 71.39; H, 9.59%).

Typical Procedure for the Denitration of Tertiary Nitro Compounds.—3-*Acetoxy*-4-*ethylcyclohexane* (**8a**). A mixture of compound (**7a**) (1.07 g, 5 mmol), Bu_3SnH (1.75 g, 6 mmol), and AIBN (0.17 g, 1 mmol) in benzene (5 ml) was heated at 80 °C for 2 h. The reaction mixture was then subjected to column chromatography (silica gel; benzene–hexane) and Kugelrohr distillation to give compound (**8a**) (0.56 g, 67%), which was analysed by g.l.c. and n.m.r. spectroscopy to be a mixture of two stereoisomers, ratio 75:25, $\nu_{max.}$ 1 725 cm^{-1}; δ (100 MHz; $CDCl_3$) 0.90 (t, 3 H, Me), 1.0—1.7 (m, 5 H, $CHCH_2CH_2$), 1.96 and 1.98 (two s, 3 H, Ac, *cis* and *trans*), 1.9—2.2 (m, 2 H, CH_2), 4.84—5.00 and 5.02—5.16 (m, 1 H, C*H*OAc), 5.5—5.9 (m, 2 H, CH=C) (Found: C, 71.05; H, 9.8. $C_{10}H_{16}O_2$ requires C, 71.39; H, 9.59%). Other adducts were treated with Bu_3SnH in the same way. Purification was achieved by column chromatography and distillation.

1-(4-*Methylpent*-3-*enyl*)*cyclohexene* (**3c**). δ (100 MHz; $CDCl_3$) 1.58 (s, 3 H, Me), 1.63 (s, 3 H, Me), 1.25—2.20 [m, 12 H, $(CH_2)_2$, $(CH_2)_4$], 5.05 (m, 1 H, CH=), and 5.35 (m, 1 H, CH=). These data are in good agreement with those reported.[4]

4-*Acetoxymethyl*-1-*methylcyclohexene* (**5b**). $\nu_{max.}$ 1 635 and 1 735 cm^{-1}; δ (100 MHz; $CDCl_3$) 1.2—2.2 (m, 7 H, CH_2CH_2-$CHCH_2$), 1.62 (s, 3 H, Me), 1.96 (s, 3 H, Ac), 3.95 (d, 2 H, *J* 8 Hz, CH_2OAc), and 5.16—5.32 (m, 1 H, CH=) (Found: C, 71.1; H, 9.75. $C_{10}H_{16}O_2$ requires C, 71.39; H, 9.59%).

4-*Butyl*-1-*methylcyclohexene* (**3d**). δ (100 MHz; $CDCl_3$) 0.88 (t, 3 H, *J* 8 Hz, Me), 1.0—2.2 [m, 13 H, $(CH_2)_3CH(CH_2)_3$], 1.58 (s, 3 H, Me), and 5.14—5.30 (m, 1 H, CH=) (Found: M^+, 152.0362. $C_{11}H_{20}$ requires *M*, 152.0364).

5-*Butyl*-1-*methylcyclohexene* (**4d**). δ (100 MHz; $CDCl_3$) 0.88 (t, 3 H, *J* 8 Hz, Me), 1.0—2.3 [m, 13 H, $(CH_2)_3CH(CH_2)_3$], 1.60 (s, 3 H, Me), and 5.12—5.30 (m, 1 H, CH=) (Found: M^+, 152.0358. $C_{11}H_{20}$ requires *M*, 152.0364). Compounds (**3d**) and (**4d**) were analysed by g.l.c. and found to be present as one regioisomer.

4-*Benzyl*-1-*methylcyclohexene* (**3e**). δ (100 MHz; $CDCl_3$) 1.58 (s, 3 H, Me), 1.2—2.15 [m, 7 H, $(CH_2)_2CHCH_2$], 2.50 (d, 2 H, *J* 8 Hz, CH_2Ph), 5.10—5.30 (m, 1 H, CH=C), and 6.90—7.26 (m, 5 H, ArH) (Found: C, 90.0; H, 9.65. $C_{14}H_{18}$ requires C, 90.26; H, 9.74%).

5-*Benzyl*-1-*methylcyclohexene* (**4e**). δ (100 MHz; $CDCl_3$) 1.60 (s, 3 H, Me), 1.2—2.3 [m, 7 H, $(CH_2)_2CHCH_2$], 2.50 (d, 2 H, *J* 8 Hz, CH_2Ph), 5.12—5.32 (m, 1 H, CH=), and 7.0—7.3 (m, 5 H, ArH) (Found: C, 90.1; H, 9.6. $C_{14}H_{18}$ requires C, 90.26; H, 9.74%).

4-*Acetoxymethyl*-5-*butyl*-1-*methylcyclohexene* (**6d**). $\nu_{max.}$ 1 740 cm^{-1}; δ (100 MHz; $CDCl_3$) 0.58 (t, 3 H, *J* 8 Hz, Me), 1.2—2.3 [m, 12 H, $(CH_2)_3CHCHCH_2CH_2$]. 1.58 (s, 3 H, Me), 1.98 (s, 3 H, Ac), 3.66—4.12 (m, 2 H, CH_2O), and 5.12—5.38 (m, 1 H, CH=) (Found: C, 74.85; H, 10.9. $C_{14}H_{24}O_2$ requires C, 74.95; H, 10.78%).

3-*Acetoxy*-4-*benzylcyclohexene* (**8c**). $\nu_{max.}$ 1 725 cm^{-1}; δ (100 MHz; $CDCl_3$) 1.30—1.70 (m, 1 H, CH), 1.92 and 1.98 (two singlets, 3 H, Ac), 1.92—2.92 (m, 6 H, CH_2CH_2, CH_2Ph), 4.98 (m, 1 H, C*H*OAc), 5.42—5.95 (m, 2 H, CH=CH), and 6.94—7.34 (m, 5 H, ArH). The *trans-cis* ratio was determined by integration of two peaks at δ 1.92 and 1.98 and was found to be 65:35 (Found: C, 78.15; H, 7.9. $C_{15}H_{18}O_2$ requires C, 78.23; H, 7.80%).

3-*Acetoxy*-5-*isopropylcyclohexene* (**8d**). $\nu_{max.}$ 1 715 cm^{-1}; δ (100 MHz; $CDCl_3$) 0.90 (d, 6 H, *J* 8 Hz, CMe_2), 1.2—2.3 [m, 6 H, $CHCH(CH_2)_2$], 2.00 (s, 3 H, Ac), 5.10—5.28 (m, 1 H), and 5.58—6.06 (m, 2 H, CH=CH) (Found: C, 72.15; H, 9.9. $C_{11}H_{18}O_2$ requires C, 72.49; H, 9.95%). Compound (**8d**) was a single stereoisomer.

4-*Ethyl*-3-*Phenylcyclohexanone* (**8e**). $\nu_{max.}$ 1 715 cm^{-1}; δ (100 MHz; $CDCl_3$) 0.96 (t, 3 H, *J* 8 Hz, Me), 1.00—1.54 (m, 3 H, CH_2CH), 1.70—2.04 (m, 2 H, CH_2), 2.04—2.80 (m, 4 H, CH_2COCH_2), 3.18—3.42 (m, 1 H, C*H*Ph), and 6.90—7.34 (m, 5 H, ArH). A *trans-cis* mixture was obtained, the ratio of which was determined by g.l.c. to be 65:35. Elemental analysis was performed after conversion into the 2,4-dinitrophenylhydrazone, m.p. 138—140 °C (Found: C, 63.0; H, 5.75; N, 14.8. $C_{20}H_{22}N_4O_4$ requires C, 62.82; H, 5.84; N, 14.65%).

5-*Ethyl*-3-*phenylcyclohexanone* (**8f**). δ (100 MHz; $CDCl_3$) 0.90 (t, 3 H, *J* 8 Hz, Me), 1.1—2.6 [m, 9 H, CH_2CHCH_2, CH_2COCH_2], 2.90 (m, 1 H, C*H*Ph), 7.1—7.4 (m, 5 H, ArH). G.l.c. analysis showed that this compound consisted of one stereoisomer (*trans*). The 2,4-dinitrophenylhydrazone had m.p. 50—51 °C (Found: C, 62.65; H, 5.75; N, 14.6. $C_{20}H_{22}N_4O_4$ requires C, 62.82; H, 5.80; N, 14.65%).

4-*Ethyl*-3-*methoxy*-5-*methylcyclohexanone* (**8g**). $\nu_{max.}$ 1 720 cm^{-1}; δ (100 MHz; $CDCl_3$) 0.95 (t, 3 H, *J* 8 Hz, Me), 1.05 (d, 3 H, *J* 8 Hz, Me), 1.1—2.0 (m, 4 H, CH_2CHCH), 2.0—2.6 (m, 4 H, CH_2COCH_2), 3.26 (s, 3 H, OMe), and 3.1—3.7 (m, 1 H, C*H*OMe). (Found: C, 70.35; H, 7.65. $C_{10}H_{18}O_2$ requires C, 70.55; H, 7.88). Compound (**8g**) consisted of four stereoisomers and could not be differentiated by g.l.c. and n.m.r. analysis.

5-*Ethyl*-3-*methoxy*-4-*methylcyclohexanone* (**8h**). $\nu_{max.}$ 1 720 cm^{-1}; δ (100 MHz; $CDCl_3$) 0.88 (d, 3 H, *J* 8 Hz, Me), 1.00 (t, 3 H, *J* 8 Hz, Me), 1.1—1.7 (m, 4 H, CH_2CHCH), 2.0—2.4 [m, 4 H, CH_2COCH_2], 3.28 (s, 3 H, Me), 3.2—3.5 (m, 1 H, C*H*OMe) (Found: C, 70.25; H, 7.75. $C_{10}H_{18}O_2$ requires C, 70.55; H, 7.88%). Compounds (**8g**) and (**8h**) were regioisomers, but stereochemistry could not be assigned.

7-*Methylbicyclo*[4.4.0]*dec*-8-*en*-2-*one* (**10**). $\nu_{max.}$ 1 705 cm^{-1}; δ (100 MHz; $CDCl_3$) 0.96 and 1.02 (two d, 3 H, Me), 1.1—2.5 (m, 11 H, saturated CH and CH_2), 5.3—5.7 (m, 2 H). The 2,4-dinitrophenylhydrazone had m.p. 165—169 °C (Found: C, 59.35); H, 5.85; N, 16.0. $C_{17}H_{20}N_4O_4$ requires C, 59.29; H, 5.85; N, 16.27%).

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