Stepwise Intramolecular Cycloaddition of Nitrile Oxide Equivalents Derived from the Lewis Acid-promoted Reaction of 1-Nitroalkadienes and Allylic Stannanes

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The Lewis acid-promoted reaction of 1-nitroalka-1,5-(or 1,6-)dienes with allylic stannanes has been studied. In the presence of $TiCl_4$, 1-nitrohexa-1,5-diene reacted smoothly with allyltrimethylstannane to give a diastereoisomeric mixture of 6-allyl-3a,4,5,6-tetrahydro-3*H*-cyclopent[*c*]isoxazoles, while the reaction using $AlCl_3$ as catalyst led to an allylated cyclohexanone oxime derivative in good yield. The similar reaction of 1-nitrohepta-1,6-diene, however, gave a bicyclic dihydroisoxazole irrespective of the Lewis acids employed. In the latter case, nitrile oxide equivalents derived from 1-nitroalka-1,6-dienes underwent a stepwise cycloaddition as shown by the lack of stereospecificity in the reactions of (1*E*,6*Z*)-1-nitro-7-phenylhepta-1,6-diene and (1*E*,6*Z*)-1-nitro-octa-1,6-diene.

In recent years, cycloaddition reactions of nitrile oxides with olefins have attracted increasing attention as convenient tools for natural product synthesis.[1] The rather unstable nitrile oxides[2] are commonly generated *in situ* in three major ways: dehydration of primary nitro compounds,[3] dehydrohalogenation of hydroxamoyl halides,[4] and oxidation of oximes.[5] Intramolecular cycloaddition of nitrile oxides resulting from the conjugate addition of an isocyanide to nitro alkenes has also been described.[6] We have recently reported that nitrile oxide equivalents generated from the reaction of allylstannanes with conjugated nitro olefins underwent intramolecular cycloaddition to give bicyclic dihydroisoxazoles.[7] In this paper, we present additional new findings about the behaviour of the above nitrile oxide equivalents shown in the presence of a strong Lewis acid.

Results and Discussion

In the presence of Lewis acid, conjugated nitro olefins are known to react as a good Michael acceptor with silyl enol ethers, silyl ketene acetals, and allylsilanes to give either nitro or *aci*-nitro derivatives, which are easily transformed to carbonyl compounds by the Nef reaction.[8] We have recently reported that $TiCl_4$ can convert stannyl nitronates into nitrile oxide equivalents at ambient temperatures, which then may be trapped intramolecularly by a dipolarophile situated at an appropriate position to form bicyclic dihydroisoxazoles.[7] In the presence of $AlCl_3$ instead of $TiCl_4$, however, the reaction of 1-nitrohexa-1,5-diene with allyltrimethylstannane led to cyclohexanone oxime derivatives,[7] which suggested to us that the dihydroisoxazole ring may be constructed stepwise under those acidic conditions.† Thus, with this point in mind, the reaction of allylic stannanes with a series of 1-nitroalkadienes variously substituted at the dipolarophilic double bond has been investigated.

The Lewis acid-promoted reaction of 1-nitro-6-phenylhexa-1,5-diene (3a) with allyltrimethylstannane (4) was carried out under the conditions shown in Scheme 2. By the addition of triethylamine, the $TiCl_4$-promoted reaction of (3a) and (4) led to intramolecular cycloaddition to give diastereoisomeric dihydro-

† In a strongly acidic medium, nitrostyrene is diprotonated to form an *N,N*-dihydroxyiminiumbenzyl dication, which reacts with benzene to give α,α-diphenylacetophenone oxime; see T. Ohwada, T. Ohta, and K. Shudo, *Tetrahedron*, 1987, **43**, 297.

Table 1. Preparation of 1-nitroalkadienes

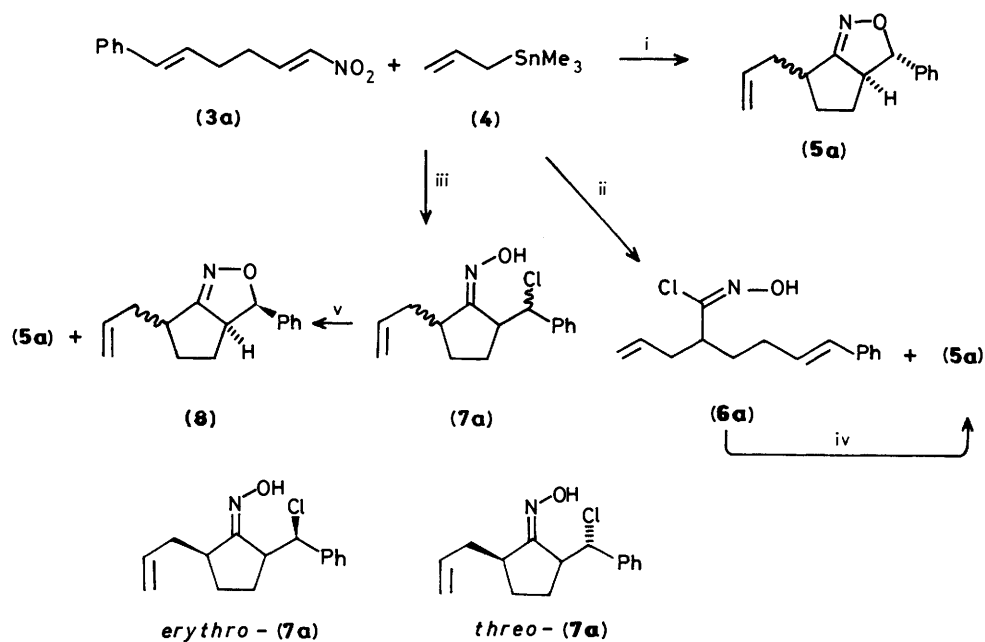| (1)	R^1	R^2	n	(2)	(3)	(*E/Z* Ratio)[a]
(a)	Ph	H	2	72	82	(5*E* > 95%)
(b)	Me	H	2	81	90	(5*E* > 95%)
(c)	H	H	3	84	75	
(d)	Me	H	3	76	81	(6*E* > 95%)
(e)	H	Me	3	70	78	(6*E*/6*Z* 17/83)
(f)	Ph	H	3	90	84	(6*E* > 95%)
(g)	H	Ph	3	94	60	(6*E*/6*Z* 56/44)[b]
(h)	Me	Me	3	64	85	
(i)[c]				69[d]	79[e]	

(Yield (%))

[a] Determined by h.p.l.c. [b] Determined by ^1H n.m.r. spectroscopy. [c] 2-(2-Methylbut-2-enyl)benzaldehyde. [d] 1-(2-Methylbut-2-enyl)phenyl]-2-nitroethanol. [e] 1-[2-(2-Methylbut-2-enyl)phenyl]-2-nitroethene.
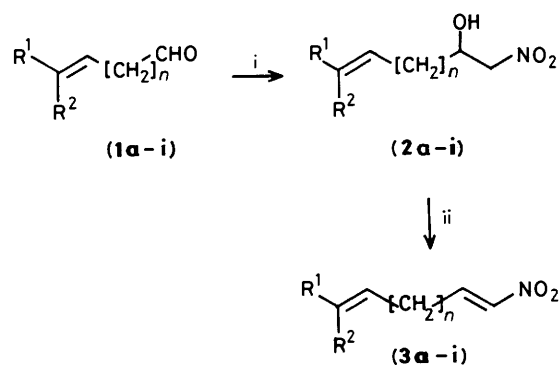

Scheme 1. *Reagents:* i, $MeNO_2$, NaOH; ii, $MeSO_2Cl$, Et_3N

isoxazoles (5a) (57:43 determined by g.l.c.) in 66% yield. Fortunately, these stereoisomers could be easily separated by column chromatography and the configuration of each isomer was determined by means of 2D n.m.r. techniques.[9] The stereochemistry between C-3 and C-3a was assigned to be *threo* by comparison of the chemical shift of C-3 proton signals with the reported values of related compounds.[10] Cross-signals attributable to ^4J-"W" coupling between 3a-H and 6-H are observed in the long-range COSY spectra of the major isomer

Scheme 2. *Reagents and conditions:* i, $TiCl_4$, CH_2Cl_2, $-78\,^\circ C$ to room temp.; then Et_3N, THF, room temp., 2 h; ii, $TiCl_4$, CH_2Cl_2, $-78\,^\circ C$ to room temp., 0.5 h; iii, $AlCl_3$, CH_2Cl_2, $-78\,^\circ C$ to room temp., 0.5 h; iv, Et_3N, CH_2Cl_2, room temp., 1 h; v, Et_3N, CH_2Cl_2, room temp., 48 h
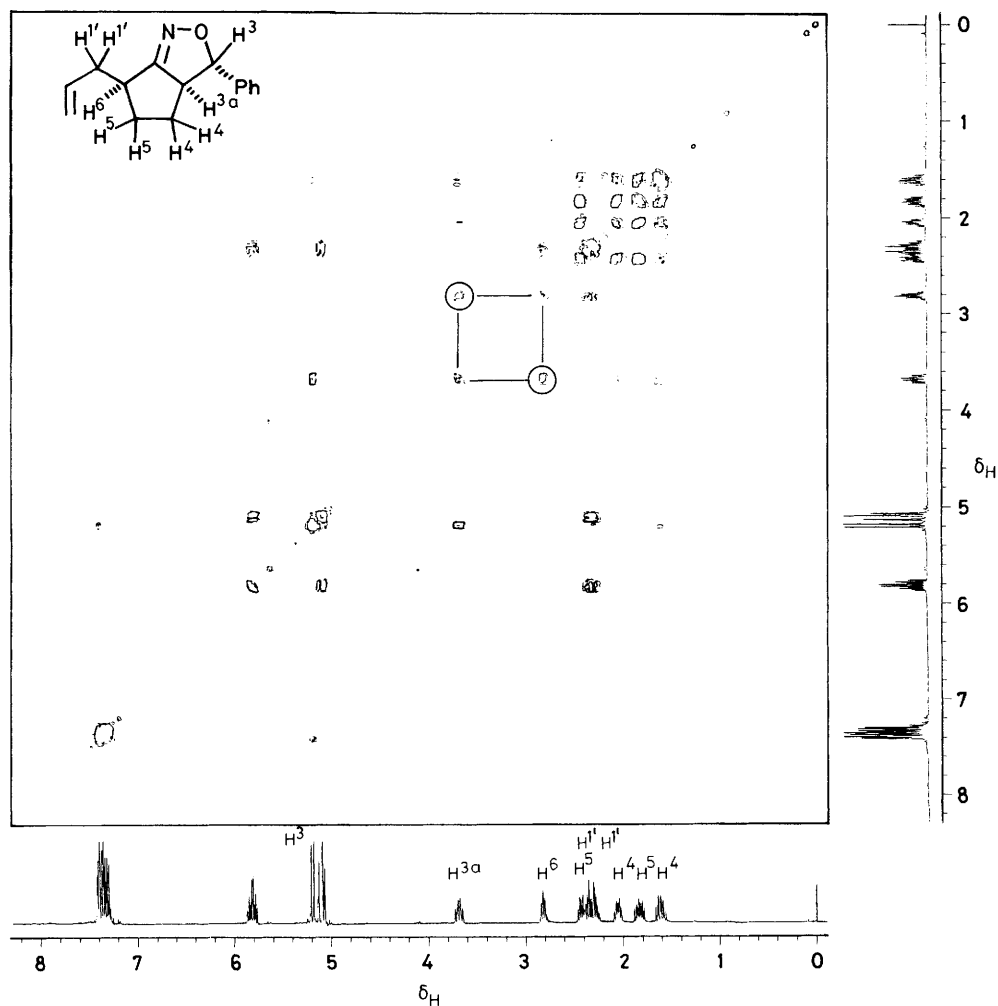
Figure. Long-range COSY spectra of major isomer of compound (5a)

(5a) (Figure). Therefore, the major isomer has a *cis* configuration between 3a-H and 6-H in accord with the structure (3a,6)-*cis*-(5a) given in the Figure.*
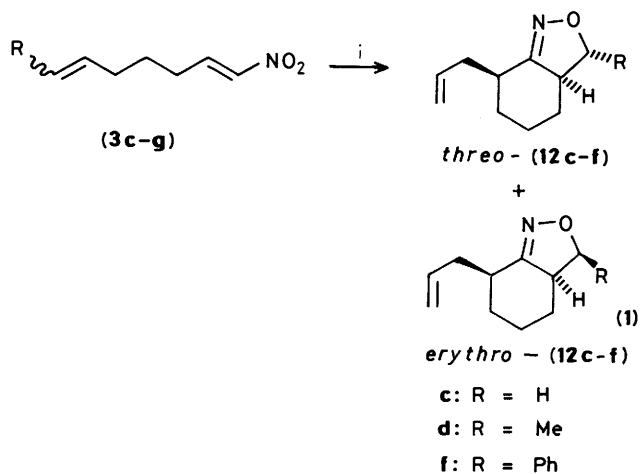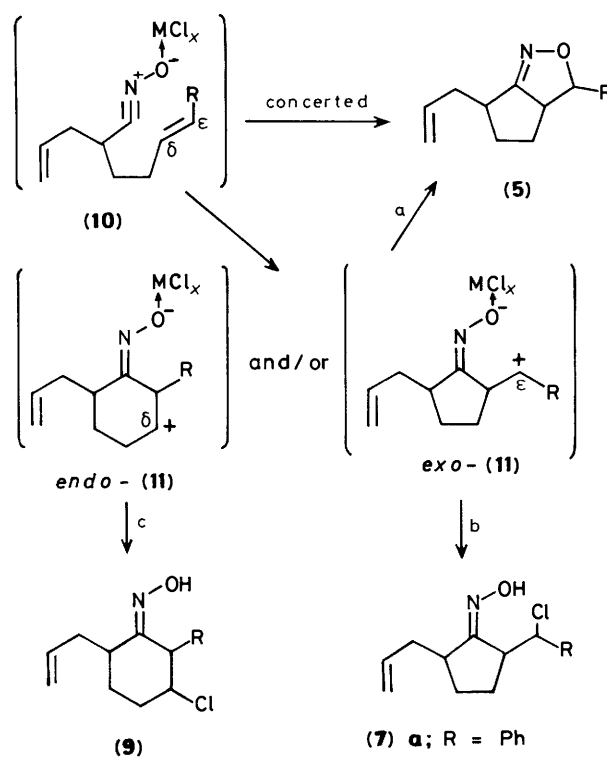
On quenching the reaction of (3a) by adding saturated aqueous NH_4Cl, we obtained hydroximic chloride (6a) as a major product (58%) together with the dihydroisoxazole (5a) (18%). The yield of (5a) increased with prolonged reaction time. Interestingly, a similar reaction using $AlCl_3$ instead of $TiCl_4$ gave mainly isomeric cyclopentanone oxime derivatives (7a). The reaction mixture was found by ^1H n.m.r. analysis to consist of four isomers of (7a) (isomer proportions 72:13:9:6) accompanied by small amounts of dihydroisoxazoles. Chromatography of this mixture over silica gel gave a mixture of only two isomeric oximes (isomer ratio 7:1) in 54% yield along with a trace of dihydroisoxazoles. The major and minor isomers of (7a) obtained were found to be the first and third ones (by amount) in the original reaction mixture. By recrystallisation from dichloromethane–hexane the major isomer was isolated and transformed stereospecifically into *cis*-(5a) on treatment with triethylamine. Since base treatment of the above mixture of (7a) (isomer ratio 5:1) in a similar manner gave *cis*-(5a) and *cis*-(8)† in the ratio 5:1, the structures of the major and minor isomers may be assigned as *erythro*- and *threo*-(7a), respectively. Conversion of the oximes (7a) into dihydroisoxazoles needed a much longer reaction time than that of (6a) into (5a). It is noteworthy that the oxime (7a) does not arise from the dihydroisoxazole (5a), since the yield of (7a) was not affected by adding (5a) to the reaction mixture. The reaction of (1*E*,5*E*)-1-nitrohepta-1,5-diene (3b) gave results similar to those of (3a), although the $AlCl_3$-promoted reaction led to an intractable mixture. As the dihydroisoxazoles (5) were obtained in the $TiCl_4$-promoted reaction of compounds (3a) and (3b) with the stannane (4) even without the base treatment, we may assume the stepwise intramolecular addition of the metalloximic chloride or nitrile oxide equivalent (10),‡ in which the resulting betaine (11) would collapse in three ways: (a) ring closure leading to the dihydroisoxazole (5a); (b) capture of a chloride ion by the electrophilic ε-carbon to give oxime (7); and (c) similar capture by the δ-carbon to give the cyclohexanone oxime (9) (Scheme 3). If the system is geometrically easier to close, the intermediacy of betaine (11) should be more important. We have already reported that the $TiCl_4$-promoted reaction of 1-nitrohepta-1,6-diene (3c) gave diastereoisomerically pure dihydroisoxazole (12c) in good yield.[7] In that case the cyclisation to the bicyclic dihydroisoxazole readily occurred under acidic conditions and treatment with base was unnecessary. Thus, we investigated the similar reactions of other 1-nitroalka-1,6-dienes without base treatment [equation (1)] and the results are summarised in Table 2.

All reactions gave bicyclic dihydroisoxazoles (12) as the only identifiable product with high stereoselectivity between C-7 and C-3a. High selectivity may be easily rationalised by assuming that an allyl group preferentially occupies the pseudo-equatorial position in a chair-like transition state. In entries 3, 4, 7, and 8 the reaction proceeded apparently in a stereo-specific manner to give *threo* isomers of (12d) and (12f). On the other hand, when (1*E*,6*Z*)-nitro-octa-1,6-diene (3e) (*E/Z* 17/83) was employed as substrate a slight decrease of stereospecificity was observed, though accompanying by-

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* No such W-coupling was detected for the minor isomer (5a). Based on the similarity of the ^{13}C n.m.r. spectra, major isomers obtained from the reaction of 1-nitrohexa-1,5-dienes with allylstannane are determined to have (3a,6)-*cis* stereochemistry; see ref. 7.

† Cross-signals between 3a-H and 6-H were also observed in the long-range COSY spectra of this compound.

‡ An equilibrium exists between hydroximic chloride and nitrile oxide (+hydrochloride); see ref. 2.

Table 2. Reaction of 1-nitro alka-1,6-dienes with compound (4)

Entry	(3)	Lewis acid	Product	Yield (%)	*threo/ erythro*
1	(3c)	$TiCl_4$	(12c)	78	
2	(3c)	$AlCl_3$	(12c)	61	
3	(3d)	$TiCl_4$	(12d)	33	>95/5[a]
4	(3d)	$AlCl_3$	(12d)	38	>95/5[a]
5	(3e)	$TiCl_4$	(12d)	49	<1/2[b]
6	(3e)	$AlCl_3$	(12d)	34	<1/3[b]
7	(3f)	$TiCl_4$	(12f)	20	>95/5[c]
8	(3f)	$AlCl_3$	(12f)	20	>95/5[c]
9	(3g)	$TiCl_4$	(12f)	34	6/1[c]

[a] Diastereoisomer ratio was determined by g.l.c. analysis of the reaction mixture. [b] See text. [c] Diastereoisomer ratio was estimated by n.m.r. spectroscopy.

endo - (11)   exo - (11)

(9)   (7) a; R = Ph

Scheme 3.

(3c–g)

threo - (12c–f)

+

(1)

erythro — (12c–f)

c: R = H
d: R = Me
f: R = Ph

Reagents and conditions: i, (4), $TiCl_4$ or $AlCl_3$, $-78\ °C$ to room temp., 2 h

products interfered with the accurate estimation of the diastereoisomeric ratios by g.l.c. In the case of diene (3g) (E/Z 64/46), the *threo*:*erythro* ratio of the product (12f) was estimated to be 6:1 by ^{1}H n.m.r. spectroscopy. Since the *threo/erythro* ratio of dihydroisoxazoles (12d) remained unchanged *even after* prolonged reaction time (2 days), and no isomerisation of the starting nitroalkadienes took place under the conditions employed,* the decrease of stereospecificity should be attributed to the stepwise construction of the dihydroisoxazole ring.

Lower yields of dihydroisoxazoles in entries 3—10 may be ascribed to the intramolecular heterodiene [4 + 2]cyclo-addition.[11] In fact, 7-methyl-1-nitro-octa-1,6-diene (3h) gave no allylated compounds but only cyclic nitronate ester (13) as an isolable product in 33% yield [equation (2)]. As nitronic esters may be regarded as 1,3-dipoles, we examined the reaction of nitronic esters and allylstannane. Although SnCl$_4$ is known to

(2)

(13)

(3)

(14)   (15)
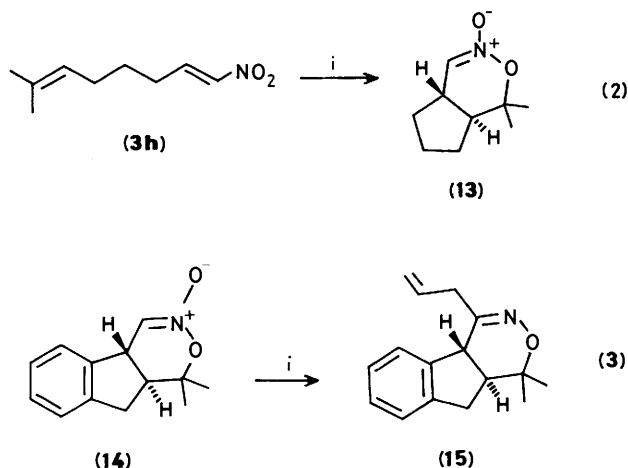
Reagents and conditions: i, (4), TiCl$_4$, −78 °C to room temp., 2 h

be the best catalyst for heterodiene [4 + 2]cycloaddition,[11] treatment of diene (3h) with SnCl$_4$ (−78 °C; 1 h) gave compound (13) only in 49% yield. Fortunately, the aromatic compound (3i) cyclised to give nitronate (14) in 80% yield, which in the presence of TiCl$_4$ reacted with allyltrimethyl-stannane (4) to give the dihydro-1,2-oxazine (15) in 30% yield [equation (3)]. Rather disappointingly, dihydro-1,2-oxazine derivatives could not be isolated from the reaction mixtures of dienes (3c—g) with the stannane (4). It is noteworthy that the higher the highest occupied orbital energy of the double bond is,[12] the more the intramolecular heterodiene [4 + 2]cyclo-addition is preferred to the intermolecular Michael addition of the allylstannane.

In conclusion, the results reported herein clearly show that in the presence of Lewis acid, nitrile oxide equivalents derived from the reaction of allylstannanes with conjugated nitro olefins undergo intramolecular cycloaddition to give bicyclic dihydro-isoxazoles. Under these strongly acidic conditions, a stepwise construction of the dihydroisoxazole ring becomes more important, especially for 1-nitroalka-1,6-dienes.

Experimental

General Methods.—M.p.s were measured with a Yanagimoto micromelting point apparatus and are uncorrected. ^{1}H N.m.r. spectra were taken on Hitachi R-600 (60 MHz), and/or JEOL-

GSX-270 (270 MHz), and/or JEOL-GX-400 (400 MHz) spectrometers with CDCl$_3$ as solvent and tetramethylsilane as internal standard. Mass spectra were obtained on a Hitachi M-80LCAPI spectrometer under the following conditions: EI (20 eV), CI (70 eV methane as CI gas), and LCAPI[13] (vaporisation temp. 330 °C, desolvation temp. 375 °C; drift voltage 155 V; needle current 6 A; mobile phase MeOH–0.1M aq. NH$_4$OAc 1:1—3:1; flow rate 0.8 ml min^{-1} column 4 × 150 mm Hitachi gel 3065 ODS 5 μm). I.r. spectra were recorded on a Hitachi 270-30 spectrophotometer. Column chromatography was performed using Wakogel C-200. Dichloromethane was distilled from calcium hydride and stored over 4 Å molecular sieves. Diethyl ether and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl and stored over sodium wire. TiCl$_4$ and SnCl$_4$ were redistilled and diluted with dry dichloromethane. Unless otherwise noted, commercially available materials were used without purification.

1-Nitroalkadienes used in this study were prepared by the modified Henry reaction as outlined in Scheme 1. Starting 4,5-unsaturated aldehydes (1a)[14] and (1b)[15] were prepared by Claisen rearrangement of the corresponding allyl vinyl ethers, while 5,6-unsaturated ones were obtained either by Wittig reaction of 2-hydroxytetrahydropyran[16] followed by oxidation with pyridinium chlorochromate (PCC)[17] [(1e),[18] (1g), and (1h)] or by one carbon homologation of 4,5-unsaturated aldehydes [(1c), (1f), and (1d)]. Configuration of unsaturated aldehydes (1a), (1b), (1f), and (1d) was determined by g.l.c. to be >95% E, consistent with E preference in thermal Claisen rearrangement.[19] Stereoisomeric E/Z ratios of (1e) and (1g) were estimated by g.l.c. to be 13/87 and 58/42, respectively. 2-(2-Methylbut-2-enyl)benzaldehyde (1i) was prepared from 2-bromobenzaldehyde according to the modified procedure reported by Hartman *et al.*[20] Condensation of nitromethane with the unsaturated aldehydes (1) gave β-nitro alcohols (2) in moderate to good yields.[21] Dehydration of alcohol (2) to (1E)-nitro alkadiene (3) was carried out using methane-sulphonyl chloride and triethylamine.[22] Double-bond migra-tion could be avoided when exactly 2 equiv. of triethylamine were used. In the preparations of nitro alkenes (3e) and (3g), a slight change of the stereoisomeric ratios occurred during chromatographic purification.

Preparation of 1-*Nitro Alcohols* (2).—General procedure for the preparation of 1-nitro alcohols (2a)—(2i) is exemplified by the preparation of 1-nitro-6-phenylhex-5-en-2-ol (2a). To an ethanolic solution (100 ml) of 5-phenylpent-4-enal (1a) (5.97 g, 37.3 mmol) and nitromethane (2.73 g, 45 mmol) was added aqueous NaOH (10% w/w; 0.6 ml) under ice cooling. After being stirred for 4 days at room temperature, the reaction mixture was quenched by the addition of water (*ca.* 100 ml) and CH$_2$Cl$_2$ (*ca.* 100 ml). The aqueous phase was acidified with acetic acid and the organic phase was separated. The aqueous phase was extracted with CH$_2$Cl$_2$ (50 ml × 2) and the combined extracts were washed successively with saturated NaHCO$_3$, water, and brine, and dried over Na$_2$SO$_4$. Evaporation of the solvent under reduced pressure gave pale yellow solids. Recrystallisation of the solids from CHCl$_3$ afforded analytically pure 1-*nitro*-6-*phenylhex*-5-*en*-2-*ol* (2a) (5.95 g, 72%) as white powdery crystals, m.p. 106—107 °C (Found: C, 64.9; H, 7.0; N, 6.1. C$_{12}$H$_{15}$NO$_3$ requires C, 65.14; H, 6.83; N, 6.33%); δ_H(60 MHz) 1.62 (2 H, m), 2.28 (2 H, m), 2.80 (1 H, br, OH), 4.33 (3 H, m), 6.13 (1 H, dt, *J* 16.7 Hz), 6.40 (1 H, d, *J* 16 Hz), and 7.27 (5 H, m); $\nu_{max.}$(KBr) 3 444s (OH), 1 642 (C=C), 1 546vs (NO$_2$), 1 384vs (NO$_2$), and 916vs cm^{-1}; *m/z* (LCAPI) 271 (M + NH$_4^+$ + MeOH, 6%), 239 (M + NH$_4^+$, 100), and 178 (45).

(E)-1-*Nitrohept*-5-*en*-2-*ol* (2b), oil, b.p. 90 °C/0.4 mmHg (kugelrohr) (Found: C, 52.6; H, 8.05; N, 8.6. C$_7$H$_{13}$NO$_3$ requires C, 52.82; H, 8.23; N, 8.80%); δ_H(60 MHz) 1.47—1.77 (6

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* 1-Phenylpent-1-ene (E/Z 68/32) added to the TiCl$_4$-promoted reaction mixture of compound (3g) was recovered intact (E/Z 65/35).

H, m), 1.93—2.30 (1 H, m), 2.63 (1 H, br, OH), 4.23—4.43 (3 H, m), and 5.27—5.60 (2 H, m); $v_{max.}$(neat) 3 428s (OH), 1 556vs (NO$_2$), and 1 384s cm^{-1} (NO$_2$); m/z (LCAPI) 209 (M + NH$_4^+$ + MeOH, 15%) and 177 (M + NH$_4^+$, 100).

1-*Nitrohept-6-en-2-ol* (**2c**), oil, b.p. 110 °C/0.3 mmHg (kugelrohr) (Found: C, 52.6; H, 8.25; N, 8.8. C$_7$H$_{13}$NO$_3$ requires C, 52.82; H, 8.23; N, 8.80%); δ_H(60 MHz) 1.53 (4 H, m), 2.08 (2 H, m), 2.76 (1 H, br, OH), 4.37 (3 H, m), 4.77—5.27 (2 H, m), and 5.70 (1 H, ddt, J 17, 9, 6 Hz); $v_{max.}$(neat) 3 444s (OH), 1 642s (C=C), 1 546vs (NO$_2$), and 1 384s cm^{-1} (NO$_2$); m/z (LCAPI) 177 (M + NH$_4^+$, 36%) and 114 (100).

(*E*)-1-Nitro-oct-6-en-2-ol (**2d**), oil, b.p. 110 °C/0.3 mmHg (kugelrohr); δ_H(60 MHz) 1.30—2.23 (9 H, m), 2.80 (1 H, br, OH), 4.20—4.57 (3 H, m), and 5.23—5.50 (2 H, m); $v_{max.}$(neat) 3 416s (OH), 1 556vs (NO$_2$), and 1 384 cm^{-1} (NO$_2$); m/z (LCAPI) 191 (M + NH$_4^+$, 89%) and 114 (100).

(*Z*)-1-*Nitro-oct-6-en-2-ol* (**2e**), 6*E*/6*Z* 13/87 mixture, oil, b.p. 110 °C/0.3 mmHg (kugelrohr) (Found: C, 52.6; H, 8.25; N, 8.8. C$_8$H$_{15}$NO$_3$ requires C, 52.82; H, 8.23; N, 8.80%); δ_H(60 MHz) 1.30—1.75 (7 H, m), 1.88—2.32 (2 H, m), 2.78 (1 H, br, OH), 4.18—4.57 (3 H, m), and 5.27—5.73 (2 H, m); $v_{max.}$(neat) 3 416s (OH), 1 556vs (NO$_2$), and 1 386 cm^{-1} (NO$_2$).

(*E*)-1-*Nitro-7-phenylhept-6-en-2-ol* (**2f**), crystals, m.p. 48—49 °C (Found: C, 66.55; H, 7.4; N, 5.9. C$_{13}$H$_{17}$NO$_3$ requires C, 66.36; H, 7.28; N, 5.95%); δ_H(270 MHz) 1.44—1.74 (4 H, m), 2.24 (2 H, q, J 6.5 Hz), 2.89 (1 H, br, OH), 4.30—4.39 (3 H, m), 6.17 (1 H, dt, J 15.6, 6.9 Hz), 6.39 (1 H, d, J 15.6 Hz), and 7.15—7.35 (5 H, m); δ_C(67.9 MHz) 24.76, 32.41, 33.04, 68.47, 80.57, 125.88, 126.96, 128.45, 129.68, 130.56, and 137.44; $v_{max.}$(neat) 3 424s (OH), 1 556vs (NO$_2$), and 1 386s cm^{-1} (NO$_2$).

(*Z*)-1-Nitro-7-phenylhept-6-en-2-ol (**2g**), 6*Z*/6*E* 58/42 mixture, oil, δ_H(270 MHz) 1.36—1.58 (4 H, m), 3.43 (1 H, m), 4.21—4.27 (3 H, m), 5.95 (1 H, dt, J 11.6 and 7.0 Hz), 6.41 (1 H, d, J 11.6 Hz), and 7.11—7.31 (5 H, m); $v_{max.}$(neat) 3 436s (OH), 1 552vs (NO$_2$), and 1 384s cm^{-1} (NO$_2$).

7-*Methyl-1-nitro-oct-6-en-2-ol* (**2h**), oil, b.p. 110 °C/0.2 mmHg (kugelrohr) (Found: C, 57.9; H, 9.2; N, 7.3. C$_9$H$_{17}$NO$_3$ requires C, 57.73; H, 9.15; N, 7.48%); δ_H(60 MHz) 1.00—2.33 (6 H, m), 1.56 (3 H, s), 1.66 (3 H, s), 2.93 (1 H, s), 3.97—4.53 (3 H, m), and 5.00 (1 H, t, J 7.0 Hz); $v_{max.}$(neat) 3 420s (OH), 1 556vs (NO$_2$), and 1 384s cm^{-1} (NO$_2$).

1-[2-(2-*Methylbut-2-enyl*)*phenyl*]-2-*nitroethanol* (**2i**), solids, m.p. <30 °C (Found: C, 66.4; H, 7.45; N, 5.8. C$_{13}$H$_{17}$NO$_3$ requires C, 66.36; H, 7.28; N, 5.95%); δ_H(60 MHz) 1.73 (6 H, m), 2.77 (1 H, d, J 3.6 Hz, OH), 3.39 (2 H, d, J 7.0 Hz), 4.43 (2 H, m), 5.13 (1 H, m), 5.60 (1 H, m), and 7.07—7.57 (4 H, m); $v_{max.}$ 3 536s, 1 556vs, 1 378s, 1 068s, and 764s cm^{-1}.

Preparation of 1-Nitro Alkadienes (**3**).—General procedure for the preparation of 1-nitro alkadienes (**3a**)—(**3i**) is exemplifed by the preparation of 1-nitro-6-phenylhexa-1,5-diene (**3a**). To a CH$_2$Cl$_2$ solution (20 ml) of alcohol (**2a**) (2.210 g, 10 mmol) and methanesulphonyl chloride (0.79 ml, 10.2 mmol) at −5 to *ca.* 0 °C was added dropwise triethylamine (2.97 ml, 20 mmol). After being stirred for 30 min, the reaction mixture was quenched by the addition of water (30 ml). The organic phase was separated and the aqueous phase was extracted with CH$_2$Cl$_2$ (20 ml × 2). The combined extracts were successively washed with water, 5% aq. HCl, water, and brine, and dried over Na$_2$SO$_4$. The solvent was evaporated off and the residue was purified by chromatography (silica gel; hexane–CHCl$_3$ as eluant) to give compound (**3a**) (1.668 g, 82%) as a yellow viscous oil, which solidified in a refrigerator (Found: C, 71.1; H, 6.5; N, 6.8. C$_{12}$H$_{13}$NO$_2$ requires C, 70.90; H, 6.45; N, 6.90%); δ_H(60 MHz) 2.2—2.45 (4 H, m), 6.03 (1 H, dt, J 17, 6 Hz), 6.33 (1 H, d, J 17.0 Hz), 6.88 (1 H, d, J 13.0 Hz), and 7.03—7.35 (6 H, m); $v_{max.}$(neat) 1 648m, 1 522s, 1 354s, 968m, and 748m cm^{-1}.

(1*E*,5*E*)-1-*Nitrohepta-1,5-diene* (**3b**), yellow oil, b.p. 80 °C/0.3

mmHg (kugelrohr) (Found: C, 59.3; H, 7.95; N, 9.7. C$_7$H$_{11}$NO$_2$ requires C, 59.56; H, 7.85; N, 9.92%); δ_H(60 MHz) 1.68 (3 H, d, J 5 Hz), 2.0—2.5 (4 H, m), 4.9—5.9 (2 H, m), 6.93 (1 H, d, J 13 Hz), and 7.17 (1 H, dt, J 13, 6 Hz); $v_{max.}$(neat) 1 648m, 1 528vs, and 1 352s cm^{-1}; m/z (LCAPI) 159 (M + NH$_4^+$, 39%), 98 (38), and 55 (100).

(1*E*)-1-*Nitrohepta-1,6-diene* (**3c**), yellow oil, b.p. 60 °C/0.18 mmHg (kugelrohr) (Found: C, 59.7; H, 7.9; N, 10.1. C$_7$H$_{11}$NO$_2$ requires C, 59.54; H, 7.86; N, 9.93%); δ_H(60 MHz) 1.4—1.88 (2 H, m), 1.88—2.57 (4 H, m), 4.77—5.17 (2 H, m), 5.65 (1 H, ddt, J 17, 9, 6 Hz), 6.95 (1 H, d, J 13 Hz), and 7.17 (1 H, dt, J 13, 6 Hz); $v_{max.}$(neat) 1 650, 1 530vs, 1 352s, and 916m cm^{-1}.

(1*E*,6*E*)-1-Nitro-octa-1,6-diene (**3d**), yellow oil, b.p. 95 °C/0.3 mmHg (kugelrohr); δ_H(60 MHz) 1.17—2.51 (9 H, m), 5.23—5.60 (2 H, m), 6.91 (1 H, d, J 13.7 Hz), and 7.27 (1 H, dt, J 13.7, 6.5 Hz); $v_{max.}$(neat) 1 650m (C=C), 1 528vs (NO$_2$), and 1 352s cm^{-1} (NO$_2$); m/z (LCAPI) 173 (M + NH$_4^+$, 100%), 156 (8), 149 (12), and 112 (43).

(1*E*,6*Z*)-1-*Nitro-octa-1,6-diene* (**3e**), yellow oil, 6*E*/6*Z* 17/83, b.p. 95 °C/0.3 mmHg (kugelrohr) (Found: C, 61.8; H, 8.5; N, 9.05. C$_8$H$_{13}$NO$_2$ requires C, 61.91; H, 8.44; N, 9.03%); δ_H(400 MHz) 1.60 (3 H, d, J 6.8 Hz), 1.62 (2 H, m), 2.11 (2 H, q, J 7.3 Hz), 2.28 (2 H, q, J 7.3 Hz), 5.30—5.60 (2 H, m), 6.99 (1 H, dd, J 13.3, 1.5 Hz), and 7.27 (1 H, dt, J 13.3, 7.3 Hz); δ_C(101 MHz) 12.49, 25.80, 27.22, 27.56, 124.87, 128.69, 139.39, and 142.19; $v_{max.}$(neat) 1 650m (C=C), 1 556vs (NO$_2$), and 1 352s cm^{-1} (NO$_2$).

(1*E*,6*E*)-1-*Nitro-7-phenylhepta-1,6-diene* (**3f**), yellow oil (Found: C, 71.7; H, 6.9; N, 6.6. C$_{13}$H$_{15}$NO$_2$ requires C, 71.87; H, 6.96; N, 6.45%); δ_H(270 MHz) 1.65 (2 H, quint, J 7.4 Hz), 2.20—2.31 (4 H, m), 6.14 (1 H, dt, J 15.9, 6.7 Hz), 6.39 (1 H, d, J 15.9 Hz), 6.95 (1 H, dt, J 13.4, 1.5 Hz), and 7.17—7.35 (6 H, m); $v_{max.}$(neat) 1 650m (C=C), 1 526vs (NO$_2$), and 1 352s cm^{-1} (NO$_2$).

(1*E*,6*Z*)-1-*Nitro-7-phenylhepta-1,6-diene* (**3g**), yellow oil, 6*E*/6*Z* 56/44 (Found: C, 71.7; H, 6.9; N, 6.6. C$_{13}$H$_{15}$NO$_2$ requires C, 71.87; H, 6.96; N, 6.45%); δ_H(270 MHz) 1.58 (2 H, m), 2.21 (2 H, m), 2.33 (2 H, qd, J 7.3, 1.5 Hz), 5.58 (1 H, dt, J 11.6, 7.3 Hz), 6.46 (1 H, d, J 11.6 Hz), 6.83 (1 H, dt, J 13.4, 1.5 Hz), and 7.10—7.35 (6 H, m); $v_{max.}$(neat) 1 648m (C=C), 1 526vs (NO$_2$), and 1 354s cm^{-1} (NO$_2$).

(1*E*)-7-*Methyl-1-nitro-octa-1,6-diene* (**3h**), yellow oil, b.p. 100 °C/0.3 mmHg (kugelrohr) (Found: C, 61.7; H, 8.8; N, 9.0. C$_9$H$_{15}$NO$_2$ requires C, 61.91; H, 8.44; N, 9.03%); δ_H(60 MHz) 1.20—2.50 (6 H, m), 1.57 (3 H, s), 1.67 (3 H, s), 5.00 (1 H, t, J 6.0 Hz), 6.81 (1 H, d, J 13 Hz), and 7.15 (1 H, dt, J 13.0, 7.0 Hz); $v_{max.}$(neat) 1 648m (C=C), 1 556vs (NO$_2$), and 1 354s cm^{-1} (NO$_2$).

(*E*)-1-[2-(2-*Methylbut-2-enyl*)*phenyl*]-2-*nitroethene* (**3i**), yellow crystals, m.p. 48—49 °C (Found: C, 72.0; H, 7.0; N, 6.3. C$_{13}$H$_{15}$NO$_2$ requires C, 71.87; H, 6.96; N, 6.45%); δ_H(60 MHz) 1.75 (6 H, m), 3.43 (2 H, d, J 7 Hz), 5.09 (1 H, m), 7.0—7.5 (4 H, m), 7.28 (1 H, d, J 13 Hz), and 8.13 (1 H, d, J 13 Hz); $v_{max.}$ 1 634s, 1 600s, 1 520vs, 968s, and 762s cm^{-1}; m/z [EI] 217 (M^+, 1.6%), 182 (5), 170 (15), 155 (84), 141 (60), and 129 (100).

TiCl$_4$-Mediated Reaction of Nitro Alkene (**3a**) *and the Stannane* (**4**) *with Subsequent Base Treatment.*—To a dry CH$_2$Cl$_2$ solution (10 ml) of compounds (**3a**) (203 mg, 1 mmol) and (**4**) (246 mg, 1.2 mmol) was added dropwise a CH$_2$Cl$_2$ solution of TiCl$_4$ (1M; 1.2 ml) at −78 °C. After the addition was complete, the reaction mixture was allowed to warm and was stirred for 2 h at room temperature. Dry THF (10 ml) and triethylamine (0.42 ml, 3 mmol) were then added to the stirred reaction mixture. After 2 h the reaction was quenched by addition of saturated aq. NaHCO$_3$ (20 ml) and ethyl acetate (20 ml). The mixture was stirred for 15 min, then filtered through a Celite pad. The pad was washed twice with ethyl acetate. The

combined organic phase was washed successively with 20% aq. KF, water, and brine, and dried over Na_2SO_4. G.l.c. analysis of the reaction mixture showed the presence of (3a,6)-*cis*-(5a) and (3a,6)-*trans*-(5a) (*cis/trans* 57/43). The solvent was removed and the residue was carefully chromatographed (silica gel; hexane–$CHCl_3$ as eluant) to give *pure bicyclo* (5a) (150 mg, 66%) as a pale yellow oil, b.p. 156 °C/0.3 mmHg (kugelrohr) (Found: C, 79.4; H, 7.6; N, 6.3. $C_{15}H_{17}NO$ requires C, 79.26; H, 7.54; N, 6.16%); $v_{max.}$(neat) 1 642w, 1 454m, 916m, 824m, and 758s cm^{-1}; *m/z* [EI] 227 (M^+, 16%), 210 (5), 168 (6), 136 (14), and 105 (100).

trans-(5a) (minor isomer from less polar eluates) was obtained as crystals, m.p. 45—50.5 °C; δ_H(400 MHz) 1.68 (1 H, m, 4-H), 2.01 (2 H, m, 4- and 5-H), 2.30 (2 H, m, 5-H and C*H*HCH=CH$_2$), 2.58 (1 H, m, CH*H*CH=CH$_2$), 2.84 (1 H, m, 6-H), 3.73 (1 H, m, 3a-H), 5.08 (1 H, m, vinyl), 5.13 (1 H, m, vinyl), 5.18 (1 H, d, *J* 11.9 Hz, 3-H), 5.92 (1 H, dddd, *J* 17.1, 10.4, 7.3, 6.4 Hz, vinyl), and 7.3—7.5 (5 H, m); δ_C(101 MHz) 25.74, 33.89, 34.61, 36.16, 61.67, 89.80, 116.58, 126.33, 128.04, 128.42, 135.72, 138.41, and 174.47.

cis-(5a) (major isomer from polar eluates) was an oil, δ_H(400 MHz) 1.61 (1 H, m, 4-H), 1.84 (1 H, m, 5-H), 2.06 (1 H, m, 4-H), 2.24—2.40 (2 H, m, C*H*$_2$CH=CH$_2$), 2.43 (1 H, m, 5-H), 2.82 (1 H, m, 6-H), 3.69 (1 H, m, 3a-H), 5.08 (1 H, m, vinyl), 5.11 (1 H, m, vinyl), 5.20 (1 H, d, *J* 11.6 Hz, 3-H), 5.82 (1 H, ddt, *J* 17.1, 10.1, 7.0 Hz, vinyl), and 7.25—7.42 (5 H, m); δ_C(101 MHz) 27.33, 34.30, 34.95, 37.16, 61.19, 89.25, 116.86, 126.13, 127.86, 128.27, 134.78, 138.32, and 174.22.

6-Allyl-3-methyl-3a,4,5,6-tetrahydro-3*H*-cyclopent-[*c*]-isoxazole, *trans*-(5b) (minor isomer) was an oil, δ_H(400 MHz) 1.47 (3 H, d, *J* 6.1 Hz, Me), 1.48 (1 H, m, 4-H), 1.88—1.98 (2 H, m, 4- and 5-H), 2.15—2.35 (2 H, m, 5-H and C*H*HCH=CH$_2$), 2.51 (1 H, m, CH*H*CH=CH$_2$), 2.78 (1 H, m, 3a-H), 4.28 (1 H, dq, *J* 12, 6.1 Hz, 3-H), 5.02—5.14 (2 H, m, vinyl), and 5.88 (1 H, dddd, *J* 17.1, 10.1, 7.3, 6.4 Hz, vinyl); δ_C(101 Hz) 18.16, 25.23, 33.93, 34.78, 36.13, 60.37, 84.59, 116.41, 135.87, and 175.25.

cis-(5b) (major isomer), δ_H(400 MHz) 1.45 (1 H, m, 5-H), 1.47 (3 H, d, *J* 6.4 Hz, Me), 1.82 (1 H, m, 4-H), 2.01 (1 H, m, 5-H), 2.20—2.35 (2 H, m, C*H*$_2$CH=CH$_2$), 2.39 (1 H, m, 4-H), 2.75 (1 H, m, 3a-H), 4.31 (1 H, dq, *J* 12, 6.4 Hz, 3-H), 5.02—5.14 (2 H, m, vinyl), and 5.79 (1 H, ddt, *J* 17.1, 10.1, 7.0 Hz, vinyl); δ_C(101 MHz) 18.16, 27.02, 34.55, 35.16, 37.34, 60.09, 84.30, 116.88, 135.07, and 175.25; $v_{max.}$(neat) 2 928s, 1 644m, 1 456m, 1 380m, 968m, and 918m cm^{-1}.

TiCl$_4$-Mediated Reaction of Compounds (3a) *and* (4) *without Base Treatment.*—To a dry CH_2Cl_2 solution (10 ml) of compounds (3a) (203 mg, 1 mmol) and (4) (246 mg, 1.2 mmol) at −78 °C was added dropwise a CH_2Cl_2 solution of TiCl$_4$ (1M; 1.2 ml). Then the stirred reaction mixture was allowed to warm to room temperature. After 30 min the reaction was quenched by the addition of saturated aq. NH$_4$Cl (20 ml). The mixture was extracted with ethyl acetate (20 ml × 3) and the combined extracts were washed successively with water and brine, and dried over Na_2SO_4. Removal of the solvent followed by column chromatography of the residue (silica gel; $CHCl_3$ as eluant) gave a pale yellow oil (183 mg, 72%) which consisted of compounds (6a) (54%) and (5a) (18%). Although separation of oxime (6a) from bicycle (5a) could be carried out by careful column chromatography on silica gel (hexane–$CHCl_3$), it could not be obtained in analytically pure state.

Compound (6a) was a pale yellow oil, δ_H(60 MHz) 1.3—2.8 (7 H, m), 4.77—5.17 (2 H, m), 5.53 (1 H, ddt, *J* 17, 9, 6 Hz), 6.00 (1 H, dt, *J* 15, 6 Hz), 6.22 (1 H, d, *J* 15 Hz), 6.9—7.3 (5 H, m), and 8.92 (1 H br, OH); $v_{max.}$(neat) 3 284s, 1 642s, 1 598m, 1 450s, 972vs, 920s, 744s, and 694s cm^{-1}.

Compound (6b) was a pale yellow oil, δ_H(60 MHz) 1.3—2.8 (7 H, m), 1.63 (3 H, m), 4.75—6.0 (5 H, m), and 8.73 (1 H, br, OH); $v_{max.}$(neat) 3 296s, 1 642m, 1 442s, 976vs, and 918s cm^{-1}.

AlCl$_3$-Mediated Reaction of Compounds (3a) *and* (4).—To a suspension of AlCl$_3$ (267 mg, 2 mmol) in dry CH_2Cl_2 (10 ml) at −78 °C was added a CH_2Cl_2 solution (1 ml) of compounds (3a) (203 mg, 1 mmol) and (4) (246 mg, 1.2 mmol). The reaction mixture was then allowed to warm up to room temperature and was stirred for 0.5 h. The reaction was quenched with aq. NH$_4$Cl. The resulting suspension was filtered through a Celite pad which was washed twice with ethyl acetate (20 ml × 2). The organic phase was washed successively with 10% aq. KF, water, and brine, and dried over Na_2SO_4. The solvent was evaporated off and the residue was chromatographed to give the product (7a) (142 mg, 54%) (isomer ratio 7:1) as a white solid together with trace amounts of dihydroisoxazoles. Recrystallisation of the isomeric mixture (7a) from dichloromethane–hexane gave *erythro*-(7a) in a pure form.

erythro-(7a) was obtained as crystals, m.p. 86—87 °C (decomp.) (Found: C, 68.2; H, 7.1; N, 5.2. $C_{15}H_{18}ClNO$ requires C, 68.30; H, 6.80; N, 5.31%); δ_H(270 MHz) 1.18 (1 H, m), 1.59 (1 H, m), 1.92—2.15 (3 H, m), 2.57—2.80 (2 H, m), 3.54 (1 H, br t, *J* 8 Hz), 5.01—5.15 (2 H, m), 5.86 (1 H, ddt, *J* 17.1, 10.1, 7.3 Hz), 6.31 (1 H, d, *J* 2.3 Hz), 7.2—7.5 (5 H, m), and 9.09 (1 H, br, OH); δ_C(67.9 MHz) 22.91, 29.60, 35.01, 44.03, 48.42, 61.90, 116.13, 126.83, 127.73, 128.29, 136.39, 140.26, and 165.88; $v_{max.}$(KBr) 3 280s, 1 454s, 964s, 940s, and 914s cm^{-1}; *m/z* [EI] 265 (M^+ + 2, 0.5%), 263 (M^+, 1.6), 226 (28), 211 (80), and 206 (100).

threo-(7a), δ_H(270 MHz, typical signals) 3.74 (1 H, br t, *J* 8 Hz), 4.90—5.05 (2 H, m), 5.66 (1 H, ddt, *J* 17.1, 10.1, 7.3 Hz), 6.15 (1 H, d, *J* 4.6 Hz), and 9.18 (1 H, br, OH); δ_C(67.9 MHz) 22.83, 28.88, 35.07, 43.41, 48.42, 60.02, 116.03, 127.96, 127.98, 128.62, 136.12, 140.26, and 165.80.

Conversion of Oxime (7a) *into Bicycle* (5a).—To a dry, stirred CH_2Cl_2 solution (10 ml) of oxime (7a) (isomer ratio 5:1; 114 mg, 0.43 mmol) was added triethylamine (0.42 ml, 3 mmol) at the room temperature and the progress of the reaction was checked by t.l.c. After 2 days all the starting material was consumed. Water (20 ml) and ethyl acetate (20 ml) was then added to the reaction mixture. The organic phase was separated and the aqueous phase was extracted with ethyl acetate (10 ml × 2). The combined extracts were washed successively with water and brine, and dried over Na_2SO_4. After the solvent was evaporated off, the residue was passed through a silica gel column with $CHCl_3$ as eluant. Evaporation of the solvent gave a mixture of *cis*-(5a) and *cis*-(8) (77 mg, 79%) [*cis*-(5a)/*cis*-(8) 5/1].

cis-(8), δ_H(270 MHz) 0.89 (1 H, m, 4-H), 1.62 (1 H, m, 4-H), 1.80 (1 H, m, 5-H), 2.20 (1 H, m, 5-H), 2.2—2.45 (2 H, m, C*H*$_2$CH=CH$_2$), 2.69 (1 H, m, 6-H), 4.12 (1 H, m, 3a-H), 5.05—5.16 (2 H, m), 5.69 (1 H, d, *J* 10.7 Hz), and 7.20—7.45 (5 H, m); δ_C(67.9 MHz) 24.16, 34.42, 35.75, 37.43, 59.27, 83.65, 117.05, 125.65, 127.45, 128.29, 135.13, 138.16, and 171.60.

TiCl$_4$-Mediated Reaction of 1-Nitro Alka-1,6-dienes with the Stannane (4).—*General procedure.* To a dry CH_2Cl_2 solution (10 ml) of a 1-nitro alka-1,6-diene (3) (1 mmol) and the stannane (4) (616 mg, 3 mmol) at −78 °C was added dropwise a CH_2Cl_2 solution (1.2 ml) of TiCl$_4$ (1 mol l^{-1}) at −78 °C. The reaction mixture was then allowed to warm and was stirred at room temperature for 2 h. The reaction was quenched with saturated aq. NaHCO$_3$ and the resulting suspension was filtered through a Celite pad. The filtrate was extracted with ethyl acetate (20 ml × 3), and the extracts were washed successively with 20% aq. KF, water, and brine, and dried over Na_2SO_4. G.l.c. analysis of the crude product was carried out at this stage. After the solvent was evaporated off, the residue was chromatographed on silica gel with hexane–$CHCl_3$ as eluant.

AlCl$_3$-Mediated Reactions of 1-Nitro Alka-1,6-dienes with the Stannane (4).—*General procedure.* To a suspension of AlCl$_3$

(271 mg, 2 mmol) in dry CH_2Cl_2 (10 ml) at -78 °C was added dropwise a CH_2Cl_2 solution (1 ml) of a 1-nitro alka-1,6-diene (3) (1 mmol) and the stannane (4) (616 mg, 3 mmol) at -78 °C. Then the stirred reaction mixture was allowed to warm up to room temperature and after 2 h was worked up as described above.

(3RS,3aSR,7SR)-7-*Allyl-3-methyl*-3,3a,4,5,6,7-*hexahydro-benz*[c]*isoxazole*, threo-(12d) was a pale yellow oil (Found: M^+, 179.1303. $C_{11}H_{17}NO$ requires M, 179.1310); δ_H(400 MHz) 1.11 (1 H, qd, J 12.5, 3.0 Hz), 1.26 (1 H, m), 1.38 (3 H, d, J 6.1 Hz), 1.40 (1 H, qt, J 12.5, 3.0 Hz), 1.86 (1 H, dq, J 13.7, 3.0 Hz), 2.05 (2 H, m), 2.18 (1 H, dt, J 14.0, 7.9 Hz), 2.27 (1 H, m), 2.63 (1 H, m), 2.69 (1 H, m), 4.17 (1 H, dq, J 9.5, 6.1 Hz), 5.0—5.1 (2 H, m), and 5.90 (1 H, m); δ_C(101 MHz) 19.59, 24.35, 31.76, 32.35, 35.37, 37.86, 55.30, 82.04, 116.26, 136.21, and 162.77; ν_{max}.(neat) 2 936s, 1 642m, 1 448s, and 1 364s cm^{-1}; m/z [EI] 179 (M^+, 100%), 178 ($M^+ - 1$, 25), 164 (14), 151 (4), and 136 (63).

(3RS,3aRS,7RS)-7-Allyl-3-methyl-3,3a,4,5,6,7-hexahydro-benz[c]isoxazole, erythro-(12d) was a pale yellow oil; δ_H(400 MHz) 1.06 (1 H, m), 1.22 (3 H, d, J 6.4 Hz), 1.1—1.25 (2 H, m), 1.82 (1 H, m), 1.90 (1 H, m), 2.05 (1 H, m), 2.19 (1 H, dt, J 14.7, 7.9 Hz), 2.32 (1 H, m), 2.70 (1 H, dt, J 14.7, 5.8 Hz), 2.99 (1 H, m), 4.68 (1 H, dq, J 10.5, 6.4 Hz), 5.0—5.1 (2 H, m), and 5.90 (1 H, ddt, J 17.1, 10.1, 7.0 Hz); δ_C(101 MHz) 15.25, 24.41, 26.43, 32.50, 35.42, 38.26, 51.35, 77.21, 116.22, 136.21, and 162.33; ν_{max}.(neat) 2 936s, 2 864s, 1 642m, 1 448s, and 1 380s cm^{-1}; m/z [EI] 179 (M^+, 100%), 178 (29), 164 (18), and 136 (42).

(3RS,3aRS,7RS)-7-*Allyl-3-phenyl*-3,3a,4,5,6,7-*hexahydro-benz*[c]*isoxazole*, threo-(12f), was a pale yellow oil (Found: C, 79.4; H, 7.9; N, 5.9. $C_{16}H_{19}NO$ requires C, 79.63; H, 7.94; N, 5.80%); δ_H(270 MHz) 1.05—1.60 (3 H, m), 1.89 (1 H, m), 2.08 (1 H, m), 2.2—2.4 (3 H, m), 2.76 (1 H, m), 3.00 (1 H, ddd, J 10.6, 9.5, 6.3 Hz), 5.03 (1 H, d, J 9.5 Hz), 5.03—5.13 (2 H, m), 5.93 (1 H, ddt, J 17.1, 10.1, 7.0 Hz), and 7.2—7.4 (5 H, m); δ_C(67.9 MHz) 24.48, 32.51, 32.53, 35.56, 38.00, 57.45, 87.69, 116.56, 125.81, 128.01, 128.66, 136.23, 140.71, and 162.37; ν_{max}.(neat) 2 928s, 2 860s, 1 642m, and 1 456s cm^{-1}; m/z [EI] 241 (M^+, 100), 240 (10), 224 (8), and 212 (4).

erythro-(12f), δ_H(270 MHz, typical signals) 0.75 (1 H, qd, J 13.0, 3.5 Hz), 0.96 (1 H, m), 1.73 (1 H, m), 3.32 (1 H, dt, J 11.0, 6.0 Hz), and 5.64 (1 H, d, J 11.0 Hz); δ_C(67.9 MHz) 24.48, 28.83, 32.43, 35.67, 38.46, 53.02, 83.29, 116.51, 126.31, 127.52, 128.25, 136.29, 138.17, and 162.00.

(4aRS,7aRS)-1,1-*Dimethyl-1*,4a,5,6,7,7a-*hexahydrocyclo-pent*[d][1,2]*oxazine N-oxide* (13), pale yellow oil; δ_H 1.36 (3 H, s), 1.44 (3 H, s), 1.62—1.83 (5 H, m), 1.99—2.12 (2 H, m), 3.00 (1 H, tt, J 8.2, 4.1 Hz), and 6.31 (1 H, d, J 3.7 Hz); ν_{max}.(neat) 2 964vs, 1 766s, 1 556s, and 1 370s cm^{-1}; m/z [EI] 169 (M^+, 11), 154 (100), 109 (25), and 67 (26); [CI] 170 ($M^+ + 1$, 38), 154 (55), 132 (12), and 71 (100).

Intramolecular Heterodiene [4 + 2]*Cycloaddition.*—To a dry CH_2Cl_2 solution (20 ml) of compound (3h) (435 mg, 2 mmol) was added dropwise a solution of $SnCl_4$ in the same solvent (2.2 ml; 1M). The reaction mixture was stirred for 1 h at this temperature and then quenched with saturated aq. NH_4Cl. The mixture was extracted with CH_2Cl_2 (20 ml × 3) and the extracts were washed successively with water and brine, and dried over Na_2SO_4. Evaporation of the solvent gave a pale yellow solid, chromatography of which gave (4aRS,9aSR)-1,1-*dimethyl*-1,4a,9,9a-*tetrahydroindeno*[1,2-d][1,2]*oxazine N-oxide* (14) as pale yellow crystals (349 mg, 80%), m.p. 137—140 °C (decomp.) (Found: C, 71.7; H, 7.1; N, 6.5. $C_{13}H_{15}NO_2$ requires C, 71.87; H, 6.96; N, 6.45%); δ_H(270 MHz) 1.33 (3 H, s), 1.53 (3 H, s), 2.77 (1 H, q, J 8.5 Hz), 3.05 (1 H, dd, J 16.0, 7.9 Hz), 3.08 (1 H, dd, J 16.0, 8.5 Hz), 4.09 (1 H, dd, J 8.2, 3.7 Hz), 6.47 (1 H, d, J 3.7 Hz), and 7.21 (4 H, m); δ_C(67.9 MHz) 23.23, 24.14, 32.91, 42.32, 43.79, 112.90, 123.69, 125.01, 127.08, 128.03, 139.40,

and 141.63; ν_{max}.(KBr) 1 606vs, 1 306s, 1 248s, 1 222s, 1 156s, 1 134s, 908s, and 780vs cm^{-1}; m/z [EI] 217 (M^+, 10%), 209 (9), 187 (10), 158 (44), 143 (93), 129 (100), and 116 (54).

(4aRS,9aSR)-4-*Allyl-1,1-dimethyl*-1,4a,9,9a-*tetrahydro-indeno*-[1,2-d][1,2]*oxazine* (15) was obtained as crystals, m.p. 63—65 °C (Found: C, 79.6; H, 8.1; N, 5.9. $C_{16}H_{19}NO$ requires C, 79.63; H, 7.94; N, 5.80%); δ_H(270 MHz) 1.29 (3 H, s), 1.34 (3 H, s), 2.67 (1 H, dt, J 11.0, 7.9 Hz, 9a-H), 2.88 (1 H, dd, J 15.6, 7.9 Hz, 9-H), 3.04 (3 H, m, $CH_2CH{=}CH_2$ and 9-H), 3.73 (1 H, d, J 8.2 Hz, 4a-H), 5.18—5.31 (2 H, m), 5.95 (1 H, ddt, J 17.1, 10.4, 7.0 Hz), 7.2 (3 H, m), and 7.37 (1 H, m); δ_C(67.9 MHz) 23.88, 25.58, 33.01 (C-9), 37.38 (4-CH_2), 41.72 (C-4a), 47.03 (C-9a), 74.31 (C-1), 118.11, 125.05, 125.73, 126.39, 127.82, 133.73, 139.89, 143.43, and 156.88; ν_{max}.(KBr) 2 976s, 1 642m, 1 478m, 1 368m, 920s, and 772s cm^{-1}; m/z [EI] 241 (M^+, 64), 224 (20), 143 (41), and 116 (100).

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