ω-Alkenyl α-Nitroalkyl Radicals. Part 3.[1,2] Radical Chain Reactions of ω-Alkenyl α-Halogenonitroalkanes

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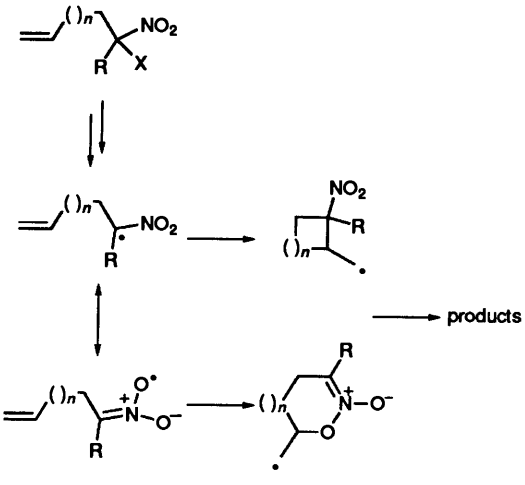
$S_{RN}1$ reactions between 5-bromo-5-nitrohex-1-ene and the nitronate anions of 2-nitropropane and 5-nitrohex-1-ene failed to give cyclisation of the intermediate α-nitroalkyl radical onto the alkene. Reaction between *exo*-5-bromo-*endo*-5-nitro-*exo*-6-phenylbicyclo[2.2.1]hept-2-ene **1** and the anion of 2-nitropropane did not undergo an $S_{RN}1$ reaction and Br^+ abstraction gave 2-bromo-2-nitropropane and 5-*endo*-nitro-*exo*-6-phenylbicyclo[2.2.1]hept-2-ene. BNAH reduction of *exo*-5-bromo-*endo*-5-nitro-*exo*-6-phenylbicyclo[2.2.1]hept-2-ene **1**, 6-bromo-6-nitrohept-1-ene, and 1-bromo-1-nitro-2-(prop-2-enyl)cyclohexane gave the corresponding nitroalkanes without any cyclisation of the intermediate α-nitroalkyl radicals. Initial results indicate that an iodine atom transfer methodology provides a possible general method for the cyclisation of ω-alkenyl α-nitroalkyl radicals. Cyclisation of intermediate α-nitroalkyl radicals, generated by photolysis of 1-(bicyclo[2.2.1]hept-5-en-*endo*-2-yl)-2-iodo-2-nitropropane **5a**, gave a good yield of two diastereoisomeric tricyclic iodonitro compounds **6a** and **7a**. Photolysis of 1-(bicyclo[2.2.1]hept-5-en-*endo*-2-yl)-2-iodo-2-nitroethane **5b** and 2-(but-3-enyl)-1-iodo-1-nitrocyclohexane **11** also gave the expected products from 5-*exo* cyclisation of the intermediate α-nitroalkyl radicals. The tricyclic iodonitro compound **6a** was synthesised from the corresponding *endo*-methanesulfonate **15**, the structure of which was determined by X-ray crystallography.

The cyclisation of alkenylalkyl radicals has been widely studied in recent years and numerous important synthetic methodologies and probes for studying radical mechanisms have been developed.[3] A large number of carbon-centred radicals have been used for cyclisation reactions onto alkenes, but the use of α-nitroalkyl radicals for cyclisation reactions had not been previously studied. With the interest in reactions proceeding *via* α-nitroalkyl radicals[4] we have undertaken a major study of the cyclisation of these radicals onto alkenes. The studies were undertaken for application to synthesis and to develop a probe for the mechanism of action of biologically active α-halogenonitroalkanes by trapping putative intermediate α-nitroalkyl radicals. The modes of action of two important antimicrobial agents, bronopol (2-bromo-1,3-dihydroxy-2-nitropropane)[5,6] and 5-bromo-5-nitro-1,3-dioxane (bronidox)[6,7] have been postulated to proceed *via* α-nitroalkyl radicals in redox reactions with microbial protein-thiol.

Intermediate α-nitroalkyl radicals can be generated by a number of well studied methods and therefore, each major method was investigated in attempts to achieve useful cyclisation reactions. The reduction of alkenyl α-halogenonitroalkanes with tributyltin hydride (Bu_3SnH)[1] and use of the oxidative addition to alkenylalkyl nitronate anions[2] have already been reported but cyclisations have only been achieved in certain limited and unusual circumstances. This final paper reports our further studies towards the cyclisation of intermediate alkenyl α-nitroalkyl radicals, generated from ω-alkenyl α-halogenonitroalkanes (Scheme 1) by means of $S_{RN}1$ reactions, reduction of α-halogenonitroalkanes with *N*-benzyl-1,4-dihydronicotinamide (BNAH), and photolysis of α-iodonitroalkanes.

Shortly after we had initiated this project, Russell and Dedolf reported[8] that $S_{RN}1$ and tributyltin hydride (Bu_3SnH) reactions of alkenyl α-halogenonitroalkanes, which proceed *via* α-nitroalkyl radicals, had failed to give cyclisation.



Scheme 1 Cyclisation of ω-alkenyl α-nitroalkyl radicals derived from ω-alkenyl α-halogenonitro compounds

Results and Discussion

Synthesis of Alkenyl Nitroalkanes.—A number of the required alkenyl nitroalkanes were synthesised using the addition of Grignard reagents to the β-position of nitroalkenes.[9,10] The method was initially tested with the addition of phenylmagnesium bromide and methylmagnesium iodide to 1-nitrocyclohex-1-ene to yield 1-nitro-2-phenylcyclohexane (90%) and 1-methyl-2-nitrocyclohexane (85%) respectively. The method was used to synthesise 1-nitro-2-(prop-2-enyl)cyclohexane (80%) and 1-nitro-2-(but-3-enyl)cyclohexane (52%) (from 1-nitrocyclohex-1-ene) and 6-nitrohept-1-ene (47%) and 5-nitrohex-1-ene (41%) (from 2-nitropropene) using the respective Grignard reagents. Other organometallic reagents can be used for addition to the β-position of nitroalkenes, *e.g.* organocadmium and organolithium derivatives, dialkylcuprates,[10] and triorganoalanes.[11]

Selective bromination and iodination involved the *in situ* formation of the nitronate anion with sodium methoxide in methanol (MeOH) and addition of *N*-bromosuccinimide or *N*-

iodosuccinimide at 0 °C. Several of the alkenyl α-iodonitroalkanes were unstable and could not be fully characterised and were used directly after rapid purification.

$S_{RN}1$ *Reactions of Alkenyl α-Bromonitroalkanes.*—$S_{RN}1$ reactions of α-substituted nitroalkanes proceed *via* α-nitroalkyl radicals and therefore provide a possible route for cyclisation onto alkenes (*e.g.* Scheme 2 with nitronates as the anions). The

$$[R_2C(X)NO_2]^{\bullet -} \longrightarrow R_2\dot{C}\text{-}NO_2 + X^- \quad (1)$$

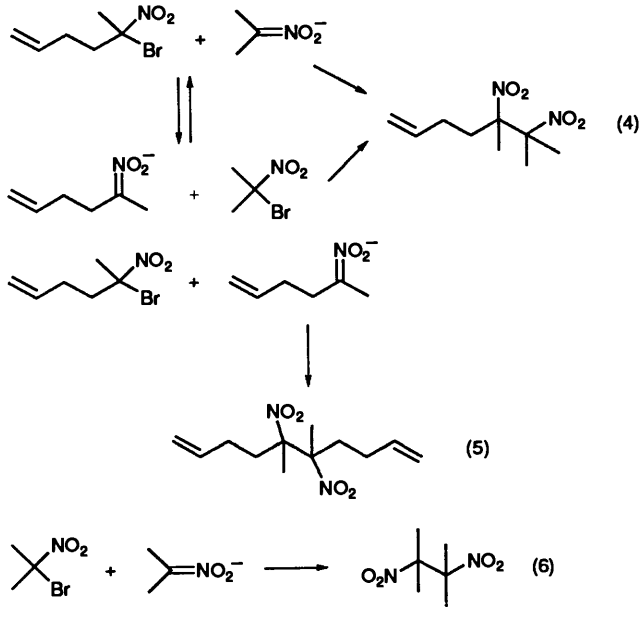
$$R_2\dot{C}NO_2 + R_2C{=}NO_2^- \longrightarrow [R_2C(NO_2)C(NO_2)R_2]^{\bullet -} \quad (2)$$

$$[R_2C(NO_2)C(NO_2)R_2]^{\bullet -} + R_2C(X)NO_2 \longrightarrow R_2C(NO_2)C(NO_2)R_2 + [R_2C(X)NO_2]^{\bullet -} \quad (3)$$

Summary: $R_2C(X)NO_2 + R_2C{=}NO_2^- \longrightarrow R_2C(NO_2)C(NO_2)R_2 + X^-$

Scheme 2 $S_{RN}1$ mechanism for the reaction between α-halogenonitroalkanes and anions of nitroalkanes

$S_{RN}1$ reactions of 6-bromo-6-nitrohept-1-ene have already been reported[8] not to proceed *via* cyclisation but earlier studies[1] using 5-bromo-5-nitrohex-1-ene had indicated that 5-*exo* cyclisation may take place *via* the O-centre of the ambident α-nitroalkyl radical (Scheme 1). Therefore, the anion of 2-nitropropane was chosen because it readily participates in $S_{RN}1$ reactions.[4,8] No cyclised products were isolated or observed in crude mixtures and three $S_{RN}1$ products were obtained from reaction between each nitronate anion with each α-bromonitroalkane (Scheme 3). The use of a lower concentration of

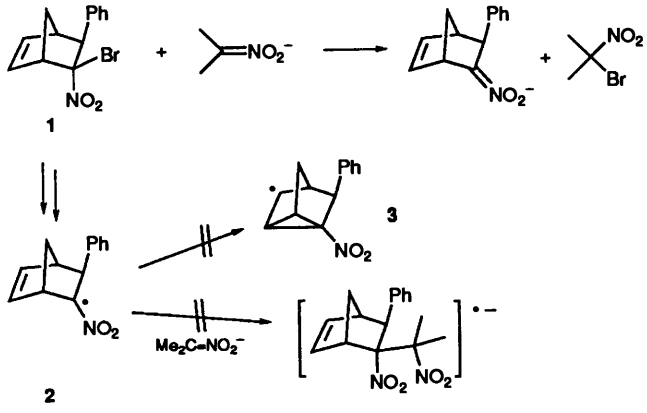


Scheme 3 The $S_{RN}1$ reactions between 5-bromo-5-nitrohex-1-ene and the anion of 2-nitropropane

reagents (0.024 mol dm^{-3}) failed to encourage unimolecular cyclisation instead of bimolecular reaction with the nucleophile [eqn. (2)]. The reaction was repeated using methanol (0.08 mol dm^{-3}) as solvent because $S_{RN}1$ reactions proceed slower in MeOH than in dipolar aprotic solvents[4] but again similar results were obtained. The mixture of products indicates that bromonium (Br^+) abstraction by the anion of 2-nitropropane is taking place [eqn. (4), Scheme 3]. The bromine is electropositive because of the strong −I effect of the α-nitro group and can be abstracted by nucleophiles.[4,8]

5-Bromo-5-nitrohex-1-ene was treated with the nitronate anion of 5-nitrohex-1-ene in order to avoid the problem of Br^+ abstraction [eqn. (4)]. 5,6-Dimethyl-5,6-dinitrodeca-1,9-diene (60%) and hex-5-en-2-one (10%) were obtained but again, no cyclised products. The $S_{RN}1$ mechanism of the reaction was investigated using standard procedures.[4,8] The addition of radical traps (oxygen and di-*tert*-butylaminoxyl) and strong electron acceptors (oxygen and *p*-dinitrobenzene) and the absence of light resulted in high inhibition of the formation of product, thus providing strong evidence for the $S_{RN}1$ mechanism. A further $S_{RN}1$ reaction between 5-bromo-5-nitrohex-2-ene and sodium benzenesulfinate, an anion commonly used in $S_{RN}1$ reactions, gave 5-phenylsulfonyl-5-nitrohex-1-ene (50%) with no cyclisation products.

The reaction between *exo*-5-bromo-*endo*-5-nitro-*exo*-6-phenylbicyclo[2.2.1]hept-2-ene **1** and the anion of 2-nitropropane was carried out under conditions favourable to the $S_{RN}1$ mechanism but only Br^+ abstraction was observed (Scheme 4). 2,3-Dimethyl-2,3-dinitrobutane was formed from

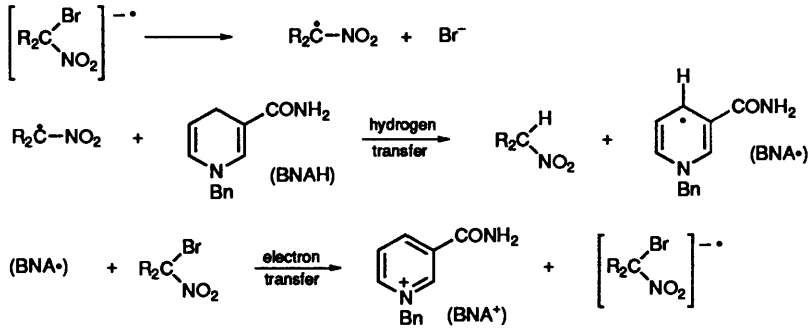


Scheme 4 Br^+ abstraction from *exo*-5-bromo-*endo*-5-nitro-*exo*-6-phenylbicyclo[2.2.1]hept-2-ene by the anion of 2-nitropropane

the reaction between 2-bromo-2-nitropropane and the anion of 2-nitropropane. Bicyclo[2.2.1]hept-2-enyl radicals have a propensity to undergo cyclisation because of the favourable orientation of molecular orbitals,[12] and the *exo*-6-phenyl-substituent should also assist cyclisation by additional buffering effects, but the intermediate radical **2** did not cyclise to **3**. The anion of 5-nitro-*exo*-6-phenylbicyclo[2.2.1]hept-2-ene formed in the reaction did not give $S_{RN}1$ products and the corresponding nitro compound (60%) was isolated after neutralisation.

Our failure to observe cyclisation during $S_{RN}1$ reactions confirms earlier research[8] and we propose that the lack of cyclisation is explained by the rapid attack by the nucleophile on the intermediate alkenyl α-nitroalkyl radicals [*e.g.* eqn. (2)], *i.e.* the rate of nucleophile addition is faster than the rate of cyclisation. The same step also forms part of the mechanism of the oxidative addition of anions onto nitronate anions for which no cyclisation was detected.[2] The rates of cyclisation[3] of various hex-5-enyl radicals range between 10^5 and 10^6 s^{-1} and the rate of addition[13] of the anions of 2-nitropropane to primary alkyl radicals is 3–9 × 10^5 dm^3 mol^{-1} s^{-1}. The addition of the anions of 2-nitropropane to the electrophilic α-nitroalkyl radicals should be considerably faster, *i.e.* faster than the rate of cyclisation. ω-Nitronate anions readily undergo cyclisation onto α-nitroalkyl radicals in oxidative addition and $S_{RN}1$ reactions[14] and the fast rate of reaction between α-nitroalkyl radicals and enamines (strongly nucleophilic alkenes)[15] indicate that to obtain cyclisation the unsaturated bond needs to be more nucleophilic than the weakly nucleophilic alkene.

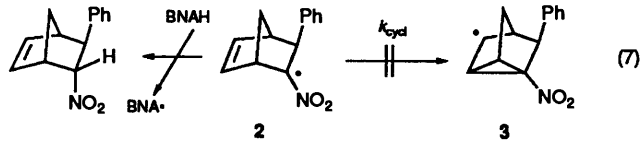
Reduction of Alkenyl α-Bromonitroalkanes with N-*Benzyl*-1,4-*dihydronicotinamide* (*BNAH*).—Although the $S_{RN}1$ studies



Scheme 5 Reduction of α-halogenonitro compounds with BNAH (Bn = CH_2Ph)

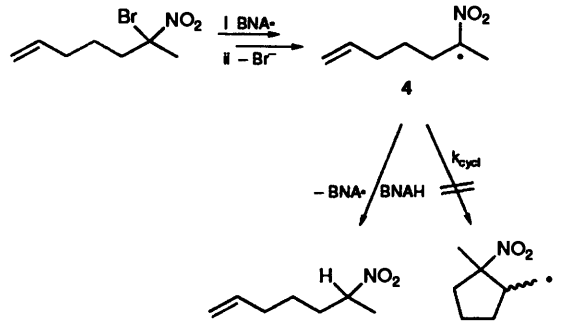
were interesting they failed to provide a method for cyclising alkenyl α-nitroalkyl radicals. Some limited success had been achieved with the Bu_3SnH reduction of α-halogenonitro compounds[1] and, therefore, another method of reduction known to proceed *via* α-nitroalkyl radicals was attempted, *i.e.* the use of *N*-benzyl-1,4-dihydronicotinamide (Scheme 5).[16–18]

The reduction of *exo*-2-bromo-*endo*-2-nitro-1,7,7-trimethylbicyclo[2.2.1]heptane (bornane derivative) with BNAH was reported to proceed in high yield.[16] We therefore used a related bicyclo[2.2.1]hept-2-ene, *exo*-5-bromo-*endo*-5-nitro-*exo*-6-phenylbicyclo[2.2.1]hept-2-ene **1**, which we hoped would undergo cyclisation because of the reported propensity of these radicals to undergo cyclisation.[12] BNAH reduction (acetonitrile solvent and photolysis) of *exo*-5-bromo-*endo*-5-nitro-*exo*-6-phenylbicyclo[2.2.1]hept-2-ene **1** gave a high yield of *endo*-5-nitro-*exo*-6-phenylbicyclo[2.2.1]hept-2-ene (96%) without any indication of products resulting from the cyclised radical intermediate **3** [eqn. (7)].



(7)

Two other substrates were also investigated with BNAH reduction. The intermediate alkenyl α-nitroalkyl radical **4**, resulting from the reduction of 6-bromo-6-nitrohept-1-ene, also failed to undergo cyclisation and 6-nitrohept-2-ene (25%) and hept-6-en-2-one (51%) were obtained (Scheme 6). The



Scheme 6 Reaction between 6-bromo-6-nitrohept-1-ene and BNAH

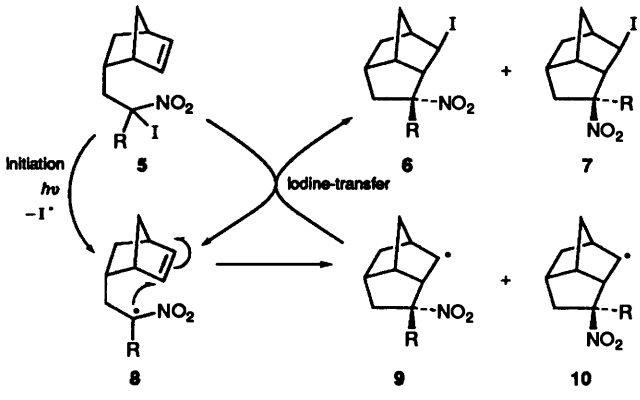
equivalent Bu_3SnH reduction yielded 6-nitrohept-1-ene (39%) and hept-6-en-2-one (2%).[1] The reaction between BNAH and 1-bromo-1-nitro-2-(prop-2-enyl)cyclohexane also failed to yield cyclisation and gave 1-nitro-2-(prop-2-enyl)cyclohexane (20%) and decomposed material.

BNAH, like Bu_3SnH, is a nucleophilic source of hydrogen, and the rate of interception of the electrophilic α-nitroalkyl radicals is faster than the rate of cyclisation. The application of electrophilic hydrogen sources, *e.g.* thiols, may provide a way forward, *i.e.* the reduction of the electrophilic α-nitroalkyl radicals could be slow and thereby allow time for cyclisation.

Photolysis of Alkenyl α-Iodonitroalkanes.—α-Iodonitroalkanes have been reported[19] to undergo photolysis to yield intermediate α-nitroalkyl radicals and iodine (I˙). The corresponding nitroalkenes, nitroalkanes and ketones are formed. The photolysis of 1-cyclopropyl-1-iodo-1-nitroethane gave cyclopropyl ring opening of the intermediate α-nitroalkyl radical indicating that this method allowed a long lifetime of the intermediate radical relative to chain transfer. In contrast, this radical had failed to undergo ring opening in $S_{RN}1$ reactions.[8]

Atom transfer reactions of α-iodo ketones, esters, malonates and malononitriles indicated the potential for cyclisation[3] and have been further developed since we carried out our studies.[20] In halogen atom transfer reactions intermediate radicals are allowed long lifetimes with respect to chain transfer but final radicals are short-lived because of fast chain transfer. Therefore, relatively slow reactions of the intermediate radicals can occur. C–I bonds are kinetically superior atom donors than are most C–H bonds. The reported[21] reaction of alkenyl α-iodo esters provides a good example of the contrast between Bu_3SnH mediated and atom transfer radical formation: Bu_3SnH (0.02 mol dm^{-3}) gives reduction with no cyclisation whereas atom transfer gives only 5-*exo* cyclisation of the intermediate alkoxycarbonyl alkyl radical.

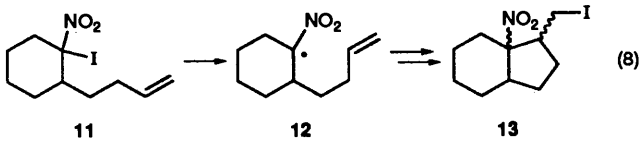
In order to provide the best chance of observing cyclisation we studied the photolysis of 1-(bicyclo[2.2.1]hept-5-en-*endo*-2-yl)-2-iodo-2-nitropropane **5a**. The 5-*exo* five-membered ring cyclisation of 2-(bicyclo[2.2.1]hept-5-en-*endo*-2-yl)ethyl radicals is especially favoured and one of the fastest reported (1×10^7 s^{-1}).[22] The photolysis of **5a** (benzene, 24 h, under nitrogen) gave two diastereoisomers, **6a** and **7a** (34%) (Scheme 7). ^1H NMR spectroscopy showed that the isomers were formed



Scheme 7 Cyclisation of α-nitro-α-(bicyclo[2.2.1]hept-5-en-*endo*-2-yl)alkyl radicals using iodine atom transfer (**a** R = Me, **b** R = H)

in a ratio of **6a**:**7a** = 45:55. We propose that the reaction proceeds by an iodine-atom transfer mechanism as observed for other similar atom transfer reactions,[21] as shown in Scheme 7. The reaction was inhibited by the radical trap, di-*tert*-butylaminoxyl, indicating a chain reaction. Complete inhibition in the absence of light shows the importance of the light initiation. The reaction follows the characteristics of atom transfer reactions, *e.g.* the intermediate cyclised radicals, **9a** and **10a**, are nucleophilic and will rapidly abstract the electrophilic iodine from the starting material **5a**. The intermediate radical **8a** is also permitted enough time to undergo cyclisation. Sterically iodine abstraction by **9a** and **10a** will only be *via* the *exo*-position of the bicyclo[2.2.1]heptane. The steric size of the methyl and nitro groups are indicated by *A*-values [Me (1.1) and nitro (1.8)],[23] which show no great preference and therefore the mixture of diastereoisomers is not unexpected. Use of propan-2-ol as solvent in place of benzene gave the same cyclised products (34%) but also yielded 1-(bicyclo[2.2.1]hept-5-en-*endo*-2-yl)propan-2-one (25%).

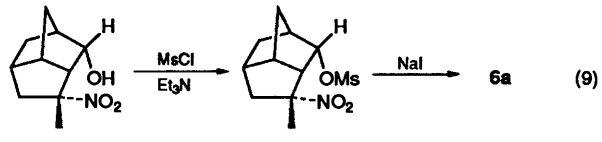
Photolysis of the equivalent primary α-iodonitroalkanes **5b** gave two diastereoisomers, **6b** and **7b** (as indicated by ^{1}H NMR spectroscopy of the crude product), but only one diastereoisomer was obtained after chromatography. Steric control by *exo*-protonation would suggest that the product would be *endo*-nitro diastereoisomer **6b** but our data does not prove this stereochemistry. Most importantly, this reaction indicates that the atom transfer method can also be applied to cyclisation of primary as well as secondary α-nitroalkyl radicals. Cyclisation of 1-iodo-1-nitro-2-(prop-2-enyl)cyclohexane gave only the corresponding nitroalkane, 1-nitro-2-(prop-2-enyl)cyclohexane. However, photolysis of 2-(but-3-enyl)-1-iodo-1-nitrocyclohexane **11** gave the expected product from 5-*exo* cyclisation **13** of the intermediate α-nitroalkyl radical **12** [eqn. (8)] as well as the corresponding nitroalkane. The iodo product **13** was unstable and could not be fully characterised.



(8)

11 **12** **13**

Structure Determination of Tricyclic Iodonitro Compound **6a**.—The known tricyclic hydroxynitro compound **14**[2] was converted into the nitro methanesulfonate **15** which was treated with sodium iodide to yield the *exo*-iodonitro **6a** [eqn. (9)].



(9)

14 **15**

The latter was not suitable for X-ray crystallography so the structure of the nitro methanesulfonate was determined instead (Fig. 1).

Formation of Ketones.—Ketones were identified as products in a number of the reactions in this study and their formation from reactions proceeding *via* intermediate α-nitroalkyl radicals has also been reported in numerous studies.[1,2,4,12,19,24,25] Rearrangement of the intermediate α-nitroalkyl radical to a cyclic oxaziridine aminoxyl which subsequently breaks down with elimination of nitric oxide to yield the corresponding ketone has been proposed.[1,12,19,24]

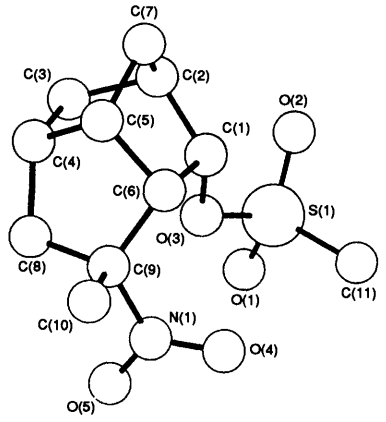


Fig. 1 Molecular structure of nitro methanesulfonate **15** with atom numbering

Conclusions.—Our initial results indicate that the iodine atom transfer methodology provides a possible general method for the cyclisation of alkenyl α-nitroalkyl radicals (primary and secondary radicals). Optimisation of the photolysis conditions and use of catalytic hexabutylditin are two possible improvements to the methodology. We suggest that our studies with alkenyl α-nitroalkyl radicals in this and the two previous papers[1,2] indicate that the reason for lack of cyclisation in Bu_3SnH and BNAH reductions, $S_{RN}1$ reactions, and oxidative additions is that the interception of the electrophilic α-nitroalkyl radicals by nucleophilic species is faster than the rate of cyclisation.

Experimental

General.—^{1}H NMR spectra were measured using a Varian EM360 spectrometer at 60 MHz unlesss otherwise stated, and at 90 MHz using a Perkin-Elmer R32. ^{13}C NMR spectra were measured using a Bruker WP-80 spectrometer at 20.1 MHz unless otherwise stated. All NMR spectra were recorded with $CDCl_3$ as solvent and tetramethylsilane (TMS) as the internal reference. *J* Values are given in Hz. *p*-Dimethoxybenzene or *p*-dinitrobenzene were used as internal standards to measure yields of products in mixtures by ^{1}H NMR spectroscopy. IR spectra were determined using either a Perkin-Elmer 177 or a Philips PU9500 spectrometer and are neat films unless otherwise stated. COSY correlation studies were obtained using a Bruker AMX 400 spectrometer at The Boots Company PLC, Nottingham. Mass spectra were recorded using a Kratos MS80 system. TLC, flash sinter, and column chromatography were carried out using silica gel as absorbent with mixtures of light petroleum and CH_2Cl_2 as eluent unless otherwise stated. Solvents were purified and dried by standard procedures. Light petroleum refers to the b.p. 40–60 °C fraction. Anhydrous magnesium sulfate was used for drying extraction solvents. Deoxygenation of reaction mixtures was achieved by purging with dry nitrogen for 1 h prior to reaction initiation. Combustion analyses were performed by the Microanalytical Department of Manchester University. Tungsten 'white light' fluorescent lamps (2 × 150 W) were used for irradiation studies.

Materials.—5-Nitrohex-1-ene,[2] 2-nitropropene,[26,27] *endo*-5-nitro-*exo*-6-phenylbicyclo[2.2.1]hept-2-ene,[2] and 1-(bicyclo-[2.2.1]hept-5-en-*endo*-2-yl)-2-nitropropane[2,28] were synthesised by the literature procedures. 1-Nitrocyclohex-1-ene and 4-bromobut-1-ene were purchased. The sodium salt of 2-nitropropane was prepared by reaction of 2-nitropropane with sodium methoxide in methanol and evaporation of methanol to dryness to give a white solid which was used without further

purification. *N*-Benzyl-1,4-dihydronicotinamide was prepared by reduction of *N*-benzylnicotinamide with sodium dithionite by literature procedures.[18,29] *N*-Benzylnicotinamide was prepared by reaction between benzyl chloride and nicotinamide.

Synthesis of Alkenyl Nitroalkanes by Reaction Between Grignard Reagents and Nitroalkenes.—General procedure. The Grignard reagents were prepared by standard methods. The Grignard reagent (1.2 equiv.) was added dropwise to a solution of the nitroalkene (0.5 g per 8 cm^3 THF) at −20 °C. The mixture was stirred for 24 h allowing slow warming to room temperature, and then quenched at −20 °C by the addition of an excess of saturated aqueous hydroxyammonium chloride. After stirring for 2 h at room temperature, the layers were separated and the aqueous layer extracted with diethyl ether. The organic fractions were combined, washed with water, dried and then evaporated to dryness to yield the crude alkenyl nitroalkane. The residues were purified using flash sinter chromatography.

(a) 1-*Nitro*-2-*phenylcyclohexane.* Phenylmagnesium bromide was treated with 1-nitrocyclohex-1-ene to yield 1-*nitro*-2-*phenylcyclohexane* (90%), m.p. 64–64.5 °C (light petroleum) (Found: C, 69.9; H, 7.4; N, 6.7. $C_{12}H_{15}NO_2$ requires C, 70.2; H, 7.3; N, 6.8%); ν_{max}/cm^{-1} 1540 and 1360; δ_H 1.70–2.30 (8 H, m), 2.95 (0.7 H, br t), 3.05 (0.3 H, br t), 4.70 (1 H, m) and 7.25 (5 H, m) [Found: M^+, 205.1102 (13%). $C_{12}H_{15}NO_2$ requires *M*, 205.1103]; *m/z* 159 ($M^+ - NO_2$, 31%) and 91 (100).

(b) 1-*Nitro*-2-*methylcyclohexane.* Methylmagnesium iodide was treated with 1-nitrocyclohex-1-ene to yield 1-methyl-2-nitrocyclohexane (85%), b.p. 100 °C/20 mmHg; ν_{max}/cm^{-1} 1545 and 1365; δ_H 0.95 (3 H, d, *J* 7), 1.35–2.05 (9 H, m) and 4.05–4.60 (1 H, m).

(c) 1-*Nitro*-2-(*prop*-2-*enyl*)*cyclohexane.* Allylmagnesium bromide was treated with 1-nitrocyclohex-1-ene to yield 1-nitro-2-(prop-2-enyl)cyclohexane (80%), b.p. 130 °C/7 mmHg; ν_{max}/cm^{-1} 3076, 1640, 1540 and 1374; δ_H 0.99–1.76 (5 H, m), 1.80–2.42 (6 H, m), 4.60 (1 H, m), 4.88 (1 H, m), 5.10 (1 H, br s) and 5.32–6.08 (1 H, m) [Found: M^+, 169.1102 (2%). $C_9H_{15}NO_2$ requires *M*, 169.1103]; *m/z* 123 ($M^+ - NO_2$, 17%) and 81 (M^+, 100).

(d) 2-(*But*-3-*enyl*)-1-*nitrocyclohexane.* But-3-enylmagnesium bromide was treated with 1-nitrocyclohex-1-ene to yield 2-(but-3-enyl)-1-nitrocyclohexane (52%), b.p. 132 °C/4 mmHg (Found: C, 65.9; H, 9.45; N, 7.8. $C_{10}H_{17}NO_2$ requires C, 65.57; H, 9.29; N, 7.65%); ν_{max}/cm^{-1} 3076, 1638, 1542 and 1376; δ_H 1.05–1.75 (6 H, m), 1.8–2.37 (7 H, m), 4.60 (1 H, m), 4.75–5.20 (2 H, m) and 5.25–6.15 (1 H, m) [Found: $M^+ - NO_2$, 137.1329 (13%). $C_{10}H_{17}NO_2$ requires $M^+ - NO_2$, 137.1330]; *m/z* 107 (16%), 95 (100) and 81 (94).

(e) 5-*Nitrohex*-1-*ene.* Allylmagnesium bromide was treated with 2-nitropropene to yield 5-nitrohex-1-ene (41%); ν_{max}/cm^{-1} 1640, 1550 and 1360; δ_H 1.52 (3 H, d, *J* 6.5), 1.60–2.05 (4 H, m), 4.53 (1 H, m), 4.95–5.25 (2 H, m) and 5.60 (1 H, m). The spectra were identical with those of authentic material.[2]

(f) 6-*Nitrohept*-1-*ene.* But-3-enylmagnesium bromide was treated with 2-nitropropane to yield 6-nitrohept-1-ene (47%); ν_{max}/cm^{-1} 3076, 1550 and 1384; δ_H 1.53 (3 H, d, *J* 6.0, Me), 1.05–2.43 (6 H, m), 4.50 (1 H, m, $CHNO_2$), 4.80–5.20 (2 H, m, alkene-H) and 5.30–6.50 (1 H, m). The spectra were identical with those of authentic material.[8]

1-(*Bicyclo*[2.2.1]*hept*-5-*en*-endo-2-*yl*)-2-*nitroethane.*—The synthesis was carried out using the reported procedure for the analogue, 1-(bicyclo[2.2.1]hept-5-en-*endo*-2-*yl*)-2-nitropropane.[14]

(a) *Henry reaction.*[14,30] Bicyclo[2.2.1]hept-5-ene-*endo*-2-carbaldehyde (1 equiv.) and potassium fluoride (0.05 equiv.) were stirred in propan-2-ol (3 equiv.) at room temperature. 2-Nitroethane (1.2 equiv.) was added dropwise and the mixture stirred for 24 h until complete as monitored by TLC. The reaction mixture was poured onto water and extracted with diethyl ether. The organic fractions were combined, dried and then evaporated to dryness. The residue was purified by flash sinter chromatography to give a colourless oil of the Henry adduct, 1-(*bicyclo*[2.2.1]*hept*-5-*en*-endo-2-*yl*)-2-*nitroethan*-1-*ol* (85%) (Found: C, 58.9; H, 7.3; N, 7.6. $C_9H_{13}NO_3$ requires C, 59.0; H, 7.1; N, 7.65%); ν_{max}/cm^{-1} 3536, 3056, 1628, 1548 and 1384; δ_H 1.00–2.45 (5 H, m), 2.60–3.00 (3 H, m), 3.70 (1 H, m, broadens on D_2O exchange, OH), 4.55 (2 H, m, CH_2NO_2) and 6.25 (2 H, m, alkene-H) [Found: M^+, 183.0885 (1.4%). $C_9H_{13}NO_3$ requires *M*, 183.0895]; *m/z* 137 ($M^+ - NO_2$, 1%), 109 (2%), 91 (19%) and 66 (100%).

(b) *Dehydration of the Henry adduct.*[14,31] The Henry adduct (1 equiv.) was dissolved in CH_2Cl_2 (10 equiv.) and methanesulfonyl chloride (1.2 equiv.) was added. The mixture was cooled to 0 °C and triethylamine (3 equiv.) added dropwise whilst stirring vigorously. Approximately half way through this addition a precipitate formed and the initially colourless solution turned yellow-orange. The reaction mixture was stirred for a further 45 min at 0 °C and then poured onto ice–water. The mixture was extracted with CH_2Cl_2, the organic extracts washed with aqueous sodium hydrogen carbonate and water, dried and then evaporated to dryness to yield crude nitroalkene, 1-(bicyclo[2.2.1]hept-5-en-*endo*-2-yl)-2-nitroethene (99%); ν_{max}/cm^{-1} 3096, 3056, 1660 and 1516; δ_H 1.40–2.45 (4 H, m), 2.96 (3 H, s), 6.22 (2 H, m) and 7.20 (2 H, m).

(c) *Reduction of the nitroalkene.*[14,32] Sodium borohydride (1.2 equiv.) was added in portions to a solution of the nitroalkene (1 equiv.) in THF (25 equiv.) while keeping the temperature below 60 °C. After stirring for 1 h, water was added and the THF evaporated under reduced pressure. The aqueous residue was adjusted to pH 14 and extracted with diethyl ether. The aqueous fraction was acidified to pH 3 and extracted with CH_2Cl_2. The organic layer was separated, dried and then evaporated to dryness to give crude nitroalkene. The residue was purified by flash sinter chromatography to give alkenyl nitroalkene,1-(*bicyclo*[2.2.1]*hept*-5-*en*-endo-2-*yl*)-2-*nitroethane* (51%) (Found: C, 64.8; H, 8.2; N, 8.4. $C_9H_{13}NO_2$ requires C, 64.67; H, 7.78; N, 8.38%); ν_{max}/cm^{-1} 3056, 1610, 1548 and 1382; δ_H 1.10–2.35 (7 H, m), 2.80 (2 H, m), 4.40 (2 H, m, CH_2NO_2) and 6.05 (2 H, m, alkene-H); *m/z* 167 (M^+, 10%), 121 ($M^+ - NO_2$, 65), 79 (100) and 67 (62).

5-*Bromo*-5-*nitrohex*-1-*ene.*—A solution of the oxime of hex-5-en-2-one (1 g, 8.85 mmol) in 1,4-dioxane (5 cm^3) was added dropwise to a stirred suspension of potassium carbonate (3.7 g) and *N*-bromoacetamide (2.5 g, 2 equiv.) in water (25 cm^3) over 5 min at 0 °C. The mixture was stirred and warmed to room temperature overnight during which time its colour changed from blue-green to orange-yellow. The aqueous reaction mixture was extracted with diethyl ether and the organic fractions were combined, dried, and then evaporated to dryness to yield a red oil (2 g). Kugelrohr distillation gave 5-*bromo*-5-*nitrohex*-2-*ene* as a pale yellow oil (950 mg, 40%), b.p. 60 °C/1 mmHg (Found: C, 34.7; H, 5.0; N, 6.8; Br, 38.8. $C_6H_{10}BrNO_2$ requires C, 34.64; H, 4.84; N, 6.73; Br, 38.41%); ν_{max}/cm^{-1} 1640, 1560 and 1340; δ_H(90 MHz) 2.20 (3 H, s), 2.22 (4 H, m), 5.00 (2 H, m) and 5.60 (1 H, m) [Found: M^+, 208.9876 (2.2%) and 206.9886 (13%). $C_6H_{10}BrNO_2$ requires *M*, 208.9874 and 206.9895]; *m/z* 81 (100%).

Halogenation of ω-Alkenyl Alkylnitro Compounds.–General procedure. Sodium (1.1 equiv.) was dissolved in dry methanol and the resulting solution stirred for 15 min. The nitroalkane (1 equiv.) was added in one portion, the mixture stirred for a further 30 min, and then cooled to 0 °C. The halogenation agent

(1.1 equiv.) (*N*-bromo- or *N*-iodo-succinimide) was added and the mixture stirred until solution was complete. The methanol solution was evaporated to dryness and the resulting residue dissolved in water–diethyl ether. The organic fraction was separated, dried and then evaporated to dryness to yield crude halogeno nitro product. Purification was achieved by Kugelrohr distillation or flash sinter chromatography using TLC alumina.

(a) 6-*Bromo*-6-*nitrohept*-1-*ene*. (61%), b.p. 85 °C/5 mmHg (Found: C, 37.5; H, 5.4; N, 6.4. $C_7H_{12}BrNO_2$ requires C, 37.8; H, 5.4; N, 6.3%); ν_{max}/cm^{-1} 3030, 1640 and 1542; δ_H(90 MHz) 1.17–1.75 (2 H, m), 1.90–2.62 (4 H, m), 2.20 (3 H, s, Me), 4.82–5.20 (2 H, m) and 5.40–6.00 (1 H, m); *m/z* 142 (M^+ − Br, 10%), 95 (142 − HNO_2, 100), 67 (22) and 55 (53).

(b) 1-*Bromo*-1-*nitro*-2-(*prop*-2-*enyl*)*cyclohexane*. (85%) (Found: C, 43.8; H, 5.7; N, 5.7. $C_9H_{14}BrNO_2$ requires C, 43.6; H, 5.7; N, 5.7%); ν_{max}/cm^{-1} 3076, 1638, 1550 and 1342; δ_H(90 MHz) 1.80–3.00 (11 H, m), 4.75–5.32 (2 H, m) and 5.40–6.20 (1 H, m); *m/z* 168 (M^+ − Br, 14%), 121 (100), 67 (28) and 55 (56).

(c) exo-5-*Bromo*-endo-5-*nitro*-exo-6-*phenylbicyclo*[2.2.1]-*hept*-2-*ene*. (65%), m.p. 53–55 °C (light petroleum) (Found: C, 52.8; H, 4.15; N, 4.75. $C_{13}H_{12}BrNO_2$ requires C, 53.06; H, 4.08; N, 4.76%); ν_{max}/cm^{-1} 3060, 3030, 1602, 1544 and 1342; δ_H(90 MHz) 2.05 (1 H, br d, *J* 11, 7-H, *anti*), 2.50 (1 H, br d, *J* 11, 7-H *syn*), 3.22 (1 H, br s, 1-H), 3.80 (2 H, m, 4-H and 6-H), 6.08 (1 H, m, 2-H), 6.52 (1 H, m, 3-H) and 7.25 (5 H, br s, Ph-H); δ_C 46.53 (7-C), 46.71 (1-C), 53.45 (4-C), 102.97 (5-C), 127.12 (2-C), 128.39 (Ph-CH), 133.73 (Ph-CH), 140.04 (Ph-C) and 142.96 (Ph-CH) [Found: M^+, 295.0031 (8%). $C_{13}H_{12}BrNO_2$ requires *M*, 295.0031]; *m/z* 249 (M^+ − NO_2, 4.1%), 2.47 (M^+ − NO_2, 4.3) and 167 (100).

(d) 4-*Bromo*-4-*nitropent*-1-*ene*. (68%), b.p. 75 °C/1.5 mmHg (Found: C, 30.7, H, 4.2; N, 7.4. $C_5H_8BrNO_2$ requires C, 30.9; H, 4.1; N, 7.2%); ν_{max}/cm^{-1} 3070, 1635, 1555 and 1350; δ_H 2.35 (4 H, m), 4.90–5.10 (2 H, m) and 5.30–5.60 (2 H, m); *m/z* 113 (M^+ − HBr, 17%), 67 (100) and 51 (91).

(e) 1-(*Bicyclo*[2.2.1]*hept*-5-*en*-endo-2-*yl*)-2-*iodo*-2-*nitropropane*. (88%), ν_{max}/cm^{-1} 3056, 1624, 1544 and 1334; δ_H 0.60–3.10 (9 H, m), 2.47 (3 H, s, Me) and 6.13 (2 H, m, alkene-H); one spot by TLC.

(f) 1-(*Bicyclo*[2.2.1]*hept*-5-*en*-endo-2-*yl*)-2-*iodo*-2-*nitroethane*. (83%), ν_{max}/cm^{-1} 3052, 1640, 1550 and 1348; δ_H 0.60–3.20 (9 H, m) and 5.80–6.46 (3 H, m, alkene-H and $CHINO_2$); one spot by TLC.

(g) exo-5-*Iodo*-endo-5-*nitro*-exo-6-*phenylbicyclo*[2.2.1]*hept*-2-*ene*. (82%), ν_{max}/cm^{-1} 3060, 3028, 1600, 1536 and 1334; δ_H 2.10 (1 H, br d, *J* 11, 7-H *anti*), 2.60 (1 H, br d, *J* 11, 7-H *syn*), 3.20 (1 H, m, 1-H), 3.40 (1 H, d, 4-H), 4.00 (1 H, m, 6-H), 6.16 (1 H, m, 2-H), 6.58 (1 H, m, 3-H) and 7.40 (5 H, br s, Ph-H); one spot by TLC.

(h) 1-*Iodo*-1-*nitro*-2-(*prop*-2-*enyl*)*cyclohexane*. (65%), ν_{max}/cm^{-1} 3076, 1638, 1544 and 1336; δ_H 1.05–2.50 (11 H, m), 4.85 (1 H, m), 5.10 (1 H, m) and 5.40–6.10 (1 H, m); one spot by TLC.

(i) 2-(*But*-3-*enyl*)-1-*iodo*-1-*nitrocyclohexane*. (68%), ν_{max}/cm^{-1} 3076, 1638, 1542 and 1340; δ_H 1.10–2.70 (13 H, m), 4.80 (1 H, m), 5.05 (1 H, m) and 5.40–6.10 (1 H, m); one spot by TLC.

(j) 1-*Iodo*-1-*nitro*-2-(*prop*-2-*enyl*)*cyclohexane*. (65%), ν_{max}/cm^{-1} 3076, 1638, 1544 and 1336; δ_H 1.05–2.50 (11 H, m), 4.85 (1 H, m), 5.10 (1 H, m) and 5.40–6.10 (1 H, m); one spot by TLC.

$S_{RN}1$ *Substitution Reactions*.—(a) *Reaction between* 5-*bromo*-5-*nitrohex*-1-*ene and the sodium salt of* 2-*nitropropane*. The sodium salt of 2-nitropropane (540 mg, 4.86 mmol) was stirred in DMF (25 cm^3) and the solution deoxygenated. 5-Bromo-5-nitrohex-1-ene (0.163 mol dm^{-3}; 850 mg, 4.04 mmol) was added to it and the reaction irradiated for *ca.* 3 h (monitored by TLC). The reaction mixture was poured onto water (100 cm^3) and extracted with diethyl ether. The organic fractions were combined, washed with water, dried, and then evaporated to dryness to yield a reddish oil containing white crystals (0.8 g). Purification by column chromatography using silica gel as absorbent and light petroleum–dichloromethane as eluent gave: (a) 2,3-*dimethyl*-2,3-*dinitrobutane* (220 mg, 25%), m.p. 210–212 °C (light petroleum, lit.,[33] 215–216 °C); δ_H 1.70 (s); (b) 5,6-dimethyl-5,6-dinitrohept-1-ene (190 mg, 22%), m.p. 40 °C re-solidifies at 42 °C then melts again at 71–72 °C (light petroleum); ν_{max}/cm^{-1} 1640, 1540 and 1360; δ_H(90 MHz) 1.60–1.70 (9 H, m), 2.10 (4 H, m), 5.10 (2 H, m) and 5.70 (1 H, m); *m/z* (CI/isobutane) 217 (MH^+ − NO_2, 2%), 101 (58) and 86 (40); (c) 5,6-*dimethyl*-5,6-*dinitrodeca*-1,9-*diene* (282 mg, 28%), m.p. 112–114 °C (light petroleum) (Found: C, 56.6; H, 8.1; N, 11.0. $C_{12}H_{20}N_2O_4$ requires C, 56.3; H, 7.8; N, 10.9%); ν_{max}/cm^{-1} 1640, 1550, 1540 and 1355; δ_H(90 MHz) 1.66 (6 H, s), 2.20 (8 H, m), 5.10 (4 H, m) and 5.70 (2 H, m); δ_C 18.24 (Me), 18.70 (Me), 28.43 (C-3, C-8), 33.51 and 34.06 (C-4 and C-7), 94.29 (95.29 and 95.62 (C-5 and C-6), 116.51 (C-1, C-10) and 135.97 (C-2 and C-9); [Found: M^+, 256.1415. $C_{12}H_{20}N_2O_4$ requires *M*, 256.1423]; *m/z* 210 (M^+ − NO_2, 5%), 163 (7), 126 (56), 95 (67) and 81 (100).

The above reaction was repeated under the same conditions except that a more dilute solution of DMF (0.024 mol dm^{-3}; 170 cm^3) was used to yield a red oil (300 mg). Leaching of the oil with light petroleum yielded 2,3-dimethyl-2,3-dinitrobutane (26 mg, 4%) as insoluble white crystals, m.p. 211–213 °C (lit.,[33] 214–216 °C). Purification of the petroleum-soluble fraction by column chromatography using silica as absorbent and light petroleum–ethyl acetate (9:1) as eluent gave 5,6-dimethyl-5,6-dinitrohept-1-ene (120 mg, 14%) and 5,6-dimethyl-5,6-dinitrodeca-1.9-diene (120 mg, 12%). All three products were identical with authentic material (TLC and IR and ^1H NMR spectra). No other products were observed.

The above reaction was repeated under the same conditions except that MeOH (0.08 mol dm^{-3}; 50 cm^3) was used in place of DMF. Purification as in the previous experiment gave 2,3-dimethyl-2,3-dinitrobutane (160 mg, 26%, m.p. 211–212 °C), 5,6-dimethyl-5,6-dinitrohept-1-ene (170 mg, 19%), and 5,6-dimethyl-5,6-dinitrodeca-1.9-diene (110 mg, 11%). No other products were observed.

(b) *Reaction between* 5-*bromo*-5-*nitrohex*-1-*ene and the sodium salt of* 5-*nitrohex*-1-*ene*. The sodium salt of 5-nitrohex-1-ene was prepared as follows: sodium (200 mg) was dissolved in methanol (10 cm^3) and 5-nitrohex-1-ene (1.00 g, 7.75 mmol) was added. The mixture was stirred for 1 h at room temperature and the methanol was evaporated to dryness to give the salt as a white solid. The ^1H NMR spectrum showed no signal at δ 4.53 corresponding to the hydrogen α to the nitro group. The salt (280 mg, 1.85 mmol) was dissolved in methanol (5 cm^3) and the resulting solution was deoxygenated. 5-Bromo-5-nitrohex-1-ene (386 mg, 1.85 mmol) in methanol (2 cm^3) was added and the solution irradiated for 4 h under an atmosphere of nitrogen until complete (monitored by TLC). The reaction mixture was worked up as in part (a) to yield an orange oil (0.28 g) which crystallised on storage. Purification using flash sinter chromatography yielded 5,6-dimethyl-5,6-dinitrodeca-1,9-diene as a colourless crystalline solid (125 mg, 27%); m.p. 112–114 °C (light petroleum). The TLC, mixed m.p., and IR and ^1H NMR spectra were identical with authentic material. Analysis of the crude product using ^1H NMR with an internal standard gave a yield of 60%.

(c) *Inhibition studies of the reaction between* 5-*bromo*-5-*nitrohex*-1-*ene and the sodium salt of* 5-*nitrohex*-1-*ene*. 5-Bromo-5-nitrohex-1-ene (241 mg, 1.16 mmol) and the sodium salt of 5-nitrohex-1-ene (175 mg, 1.16 mmol) were treated as above for 2.5 h. The crude product mixture was analysed by ^1H NMR spectroscopy using an internal standard. The extent of reaction, expressed as the ratio of product (0.57 mmol) to starting

material (0.51 mmol), was 1.10. The reaction was repeated under the same conditions except that *p*-dinitrobenzene (49 mg, 0.29 mmol) was added prior to irradiation to give an extent of reaction of 0.30. A repeat experiment with di-*tert*-butylaminoxyl (37 mg, 0.29 mmol) gave an extent of reaction of 0.08. The reaction was repeated under the same conditions except that the stream of nitrogen was replaced by oxygen to give the extent of reaction as 0.12. The reaction was repeated in the absence of light by covering the reaction flask with aluminium foil to give the extent of reaction as 0.2.

(d) *Reaction between* exo-5-*bromo*-endo-5-*nitro*-exo-6-*phenylbicyclo*[2.2.1]*hept*-2-*ene and the sodium salt of* 2-*nitropropane*. *exo*-5-Bromo-*endo*-5-nitro-*exo*-6-phenylbicyclo[2.2.1]hept-2-ene (300 mg, 1.02 mmol) and the sodium salt of 2-nitropropane (135 mg, 1.2 mmol) were dissolved in DMF (15 cm^3) and the solution deoxygenated and irradiated for 3.5 h. The reaction mixture was worked up as in part (a) to yield a red-brown oil (0.25 g). ^1H NMR and GLC analysis (SGE BP1, 75 °C, isothermal) showed 2-bromo-2-nitropropane (10%), *endo*-5-nitro-*exo*-6-phenylbicyclo[2.2.1]hept-2-ene (60%), and 2,3-dimethyl-2,3-dinitrobutane (14%). The latter two products were identified by separation using flash sinter chromatography.

Reduction of Alkenyl α-Bromonitroalkanes with N-*Benzyl*-1,4-*dihydronicotinamide* (*BNAH*).—(a) exo-5-*Bromo*-endo-5-*nitro*-exo-6-*phenylbicyclo*[2.2.1]*hept*-2-*ene*. *exo*-5-Bromo-*endo*-5-nitro-*exo*-6-phenylbicyclo[2.2.1]hept-2-ene (200 mg, 0.68 mmol) was dissolved in acetonitrile (4 cm^3) and the solution deoxygenated with nitrogen. BNAH (160 mg, 0.74 mmol) was added and the solution irradiated for 6 h. The reaction mixture was evaporated to dryness and the residue partitioned between water (25 cm^3) and dichloromethane (50 cm^3). The organic layer was separated, dried, and then evaporated to dryness to yield an oil. ^1H NMR (90 MHz) and IR spectroscopy and TLC indicated the oil was pure *endo*-5-nitro-*exo*-6-phenylbicyclo-[2.2.1]hept-2-ene (140 mg, 96%).

(b) 6-*Bromo*-6-*nitrohept*-1-*ene*. BNAH (525 mg, 2.9 mmol) was added in one portion to a solution of 6-bromo-6-nitrohept-1-ene (540 mg, 2.4 mmol) in acetonitrile (81 cm^3) and irradiated for 24 h (monitored by TLC). Work-up as above yielded a crude oil (480 mg). Purification by flash-sinter chromatography gave 6-nitrohept-1-ene (86 mg, 25%) and hept-6-en-2-one (136 mg, 51%). Both compounds were identical with authentic material (^1H NMR and IR spectra and TLC). Authentic hept-6-en-2-one was prepared by a standard procedure. 4-Bromobut-1-ene was treated with the anion of ethyl 2-oxobutanoate (51%), and the resulting α-keto ester hydrolysed with aqueous sodium hydroxide. Acidification and decarboxylation yielded the required ketone (65%); ν_{max}/cm^{-1} 1712 and 1638; δ_H 1.65–2.25 (7 H, m), 2.15 (3 H, s, Me), 5.00 (2 H, m) and 5.65 (1 H, m).

(c) 1-*Bromo*-1-*nitro*-2-(*prop*-2-*enyl*)*cyclohexane*. 1-Bromo-1-nitro-2-(prop-2-enyl)cyclohexane (125 mg, 0.5 mmol) was treated as above to yield 1-nitro-2-(prop-2-enyl)cyclohexane (20%).

Photolysis of Alkenyl α-Iodonitroalkanes.—General procedure. The α-iodonitroalkanes were dissolved in benzene (0.03 mol dm^{-3}), deoxygenated, and then irradiated for 24 h. As irradiations proceeded the colour of the solutions changed from pale yellow to purple. The benzene solutions were evaporated to dryness to give dark brown oils which were redissolved in dichloromethane. The solutions were washed with 2% aqueous sodium thiosulfate and water, dried, and then evaporated to dryness to yield crude product mixtures which were purified and analysed as indicated.

(a) 1-(*Bicyclo*[2.2.1]*hept*-5-*en*-endo-2-*yl*)-2-*iodo*-2-*nitropropane* (**5a**). The iodonitroalkane (900 mg, 3 mmol) was photolysed using the general procedure. Purification of the resulting crude product by preparative TLC (CH_2Cl_2–light petroleum) gave the tricyclic iodonitro isomers **6a** and **7a** as a pale yellow oil (325 mg, 36%) (Found: C, 39.4; H, 4.7; I, 41.7; N, 4.6. $C_{10}H_{14}INO_2$ requires C, 39.1; H, 4.6; I, 41.4; N, 4.6%); ν_{max}/cm^{-1} 1530 and 1350; δ_H 0.90–2.70 (9 H, m), 1.72 (1.35 H, s, *exo*-Me) and 1.80 (1.65 H, s, *endo*-Me), 3.16 and 3.42 (1 H, 2 × br s), 3.50 (0.45 H, t, CHI with *exo*-Me) and 3.85 (0.55 H, t, CHI with *endo*-Me); δ_C 23.15 (*exo*-Me), 27.34 (CH), 28.86 (CH), 30.43 (*endo*-Me), 35.97, 36.30, 37.47, 38.02, 40.14, 40.93, 42.51, 45.24, 46.88, 47.24, 47.49, 48.21, 64.42 (CHI), 64.78 (CHI), 97.61 (CNO_2) and 99.33 (CNO_2) (Found: M^+, 307.0075. $C_{10}H_{14}INO_2$ requires *M*, 307.0071); *m*/*z* 307 (M^+, 0.14%), 261 ($M^+ - NO_2$, 14), 180 ($M^+ - I$, 28), 150 (96), 134 (22), 133 (42), 105 (23) and 93 (100).

The iodonitroalkane **5a** (375 mg, 1.2 mmol) was treated under the same conditions at 40 °C except that light was excluded by wrapping the reaction vessel in aluminium foil. Analysis of the resulting crude product (320 mg) using ^1H NMR spectroscopy with an internal standard indicated that the reaction product consisted of starting material (91%) and tricyclic iodonitro compounds **6a** and **7a** (9%). TLC confirmed that no other products were present.

Iodonitroalkane **5a** (300 mg, 1 mmol) was again photolysed under the same conditions after di-*tert*-butylaminoxyl (45 mg, 0.03 mmol) had been added to act as a radical trap. Analysis of the crude product (325 mg) using ^1H NMR spectroscopy and TLC indicated mostly starting material with a small amount of decomposed material. None of the tricyclic iodonitroalkanes **6a** and **7a** were detected.

Iodonitroalkane **5a** (850 mg, 2.8 mmol) was photolysed using the same conditions as for part (a) except that propan-2-ol was used in place of benzene as solvent. Two products were isolated from preparative TLC (CH_2Cl_2–light petroleum); tricyclic iodonitro compounds **6a** and **7a** (290 mg, 34%) and 1-(bicyclo[2.2.1]hept-5-en-*endo*-2-yl)propan-2-one (95 mg, 25%). The products were identified by comparison with authentic materials using IR and ^1H NMR spectroscopy and TLC.

(b) 1-(*Bicyclo*[2.2.1]*hept*-5-*en*-endo-*yl*)-2-*iodo*-2-*nitroethane* (**5b**). The iodonitroalkane (728 mg, 2.5 mmol) was photolysed using the general procedure to give a high yield of the expected product. Purification of the resulting crude product by preparative TLC (CH_2Cl_2–light petroleum) gave extensive decomposition but some of the tricyclic iodonitro compound **7b** was separated as a pale yellow oil (165 mg, 23%); ν_{max}/cm^{-1} 1540 and 1370; δ_H 1.05–2.50 (8 H, m), 2.80 (1 H, br s), 3.25 (1 H, br d), 3.65 (1 H, m, CHI) and 4.90 (1 H, br t, $CHNO_2$) (Found: $M^+ - NO_2$, 246.9971 and $M^+ - I$, 166.0858. $C_9H_{12}INO_2$ requires $M^+ - NO_2$, 246.9986 and $M^+ - I$, 166.0868); *m*/*z* 246 ($M^+ - NO_2$, 0.5%), 166 ($M^+ - I$, 7) and 66 (100). Accurate elemental analysis could not be achieved even though TLC showed one clean spot.

(c) 1-*Iodo*-1-*nitro*-2-(*prop*-2-*enyl*)*cyclohexane*. Photolysis of 1-iodo-1-nitro-2-(prop-2-enyl)cyclohexane (510 mg, 1.7 mmol) yielded an orange oil (320 mg). ^1H NMR spectroscopy and TLC indicated one major product, 1-nitro-2-(prop-2-enyl)cyclohexane. Purification was not carried out.

(d) 2-(*But*-3-*enyl*)-1-*iodo*-1-*nitrocyclohexane*. Purification of the crude product from the photolysis of 2-(but-3-enyl)-1-iodo-1-nitrocyclohexane (500 mg, 1.6 mmol) by preparative TLC (CH_2Cl_2–light petroleum) gave a clear oil (120 mg). TLC and ^1H NMR spectroscopy indicated 2-(but-3-enyl)-1-nitrocyclohexane as a minor component and a major component which evidence suggests is the expected cyclised product. The major component was unstable and further purification was precluded; ν_{max}/cm^{-1} 1530 and 1360; δ_H poor spectrum but included 3.13–3.30 (dd, CH_2I); δ_C 5.75 (CH_2I), 98.58 (tertiary-C-NO_2) (Found: M^+, 309.0230, $M^+ - NO_2$, 263.0281 and $M^+ - I$, 182.1184. $C_{10}H_{16}INO_2$ requires M^+, 309.0227, $M^+ - NO_2$, 263.0298 and $M^+ - I$, 182.1181); *m*/*z* 309 (M^+, 0.4%),

263 ($M^+ - NO_2$, 3.6), 182 ($M^+ - I$, 0.3), 153 (42), 135 (29) and 77 (100).

(e) exo-5-*Iodo*-endo-5-*nitro*-exo-6-*phenylbicyclo*[2.2.1]*hept*-2-*ene* (82%). TLC and ^1H NMR and IR spectra of the crude product showed a complex mixture and was not purified.

Conversion of the Tricyclic Alcohol **14** *to the Tricyclic Iodide* **6a**.—The tricyclic alcohol **14** (400 mg, 2 mmol) was dissolved in pyridine (10 cm^3) and methanesulfonyl chloride (350 mg, 3 mmol) added. This mixture was stirred at room temperature for 24 h, poured slowly onto ice–hydrochloric acid (2 mol dm^{-3}; 100 cm^3), and acidified to pH 5. The aqueous solution was extracted with dichloromethane, and the organic fractions were combined, washed with hydrochloric acid (2 mol dm^{-3}), saturated aqueous sodium hydrogen carbonate and water, dried and then evaporated to yield a pale yellow solid (450 mg). Recrystallisation gave the nitro methanesulfonate **15** as white plates (400 mg, 72%), m.p. 159–160 °C (hexane); ν_{max}/cm^{-1} 1532 and 1354; δ_H 1.00–2.80 (10 H, m) including 1.70 (3 H, s, Me), 2.95 (3 H, s, $MeSO_2$) and 5.05 (1 H, m, C*H*OMs). The structure was confirmed by X-ray crystallography (Fig. 1).

The nitro methanesulfonate **15** (400 mg, 1.4 mmol) was dissolved in acetone (10 cm^3) and heated to reflux. Sodium iodide (570 mg, 3.8 mmol) was added and the mixture maintained at reflux for 12 h. The acetone was evaporated and the resulting residue partitioned between water and dichloromethane. The organic layer was dried, and then evaporated to dryness to yield an orange oil (200 mg). ^1H NMR spectroscopy indicated **6a** (*ca.* 70%) and that *ca.* 15% of the methanesulfonate remained. Purification using preparative TLC with CH_2Cl_2–light petroleum as eluent gave the tricyclic iodonitro compound **6a** as a pale yellow oil (87 mg, 18%); ν_{max}/cm^{-1} 1530 and 1350; δ_H(90 MHz) 0.90–3.20 (10 H, m), 1.72 (3 H, s, Me) and 3.50 (1 H, t, CHI). The TLC and ^1H NMR corresponded with one of the tricyclic iodonitro isomers. The IR spectrum was very similar but not identical with the spectrum of the isomeric mixture.

Crystal data.—$C_{11}H_{17}NO_5S$, M = 275.305, monoclinic, a = 6.186(10), b = 24.278(20), c = 9.606(10) Å, β = 120.3(1)°, U = 1269.71 $Å^3$ (by optimisation of axial row reflections), space group $P2_1/c$, Z = 4, D_x = 1.441 g cm^{-3}, crystal dimensions: 1.3 × 0.4 × 0.1 mm, μ(Mo-Kα) = 2.19 cm^{-1}.

Data collection and processing. Stoe Stadi-2 Weissenberg diffractometer, ω scan, graphite monochromated Mo-Kα radiation (λ = 0.710 69 Å); 2767 reflections ($5 < 2\theta < 50$) of which 1879 observed with $F/\sigma(F) > 6.0$; standard reflection measured on each layer indicated negligible crystal decay. No correction was made for absorption.

Structure analysis and refinement. Structure solved by direct methods (SHELX76) and resolved by full-matrix least-squares based on F with unit weights. Non-H atoms were refined anisotropically and H atoms were located by difference map and not refined, final shift/error 0.001. The final R value was 0.044 for 1879 reflections and 163 refined parameters. Electron density residuals in the final difference map were $-0.03 \longrightarrow +0.02\ e^-\ Å^{-3}$. Programs and computers used are referenced in reference 34. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre.*

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* For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, 1994, Issue 1.

References

1 Part 1, W. R. Bowman, D. Crosby and P. J. Westlake, *J. Chem. Soc., Perkin Trans. 1*, 1991, 73.
2 Part 2, W. R. Bowman, D. S. Brown, C. A. Burns and D. Crosby, *J. Chem. Soc., Perkin Trans. 1*, 1993, 2099.
3 D. P. Curran, *Synthesis*, 1988, 417, 489; M. Ramaiah, *Tetrahedron*, 1987, **43**, 3541; B. Giese, *Radicals in Organic Synthesis: Formation of Carbon–Carbon Bonds*, Pergamon, New York, 1986; C. P. Jasperse, D. P. Curran and T. L. Fevig, *Chem. Rev.*, 1991, **91**, 1237; D. Crich and W. B. Motherwell, *Free-Radical Processes in Organic Synthesis*, Academic Press, London, 1991.
4 W. R. Bowman, *Chem. Soc. Rev.*, 1988, **17**, 283; W. R. Bowman, in *Photoinduced Electron Transfer*, eds. M. A. Fox and M. Chanon, Elsevier, The Hague, 1988.
5 W. R. Bowman and R. J. Stretton, *Antimicrobial Agents and Chemotherapy*, 1972, **2**, 504; S. I. Al-Khalil and W. R. Bowman, *Tetrahedron Lett.*, 1984, **25**, 461.
6 M. C. R. Symons, R. Beugelmans, W. R. Bowman and A. Lechevallier, *Tetrahedron Lett.*, 1989, **30**, 5949.
7 M. Ghannoum, M. Thompson, W. R. Bowman and S. I. Al-Khalil, *Folia Microbiol. (Prague)*, 1986, **31**, 19.
8 G. A. Russell and D. F. Dedolf, *J. Org. Chem.*, 1985, **50**, 2498.
9 G. D. Buckley and E. Ellery, *J. Chem. Soc.*, 1947, 1494, 1497; E. J. Corey and H. Estreicher, *J. Am. Chem. Soc.*, 1978, **100**, 6294.
10 P. Perlmutter, *Conjugate Addition Reactions in Organic Synthesis*, Pergamon, Oxford, 1992, pp. 303–304.
11 A. Pecunioso and R. Menicagli, *J. Org. Chem.*, 1988, **53**, 45.
12 D. I. Davies, D. J. A. Pearce and E. C. Dart, *J. Chem. Soc., Perkin Trans. 1*, 1973, 433; C. R. Warner, R. J. Strunk and H. G. Kuivila, *J. Org. Chem.*, 1966, **31**, 3381.
13 G. A. Russell and D. Guo, *Tetrahedron Lett.*, 1984, **25**, 5239.
14 W. R. Bowman and S. W. Jackson, *Tetrahedron Lett.*, 1989, **30**, 1857; *Tetrahedron*, 1990, **46**, 7313.
15 G. A. Russell and K. Wang, *J. Org. Chem.*, 1991, **56**, 3475.
16 R. J. Kill and D. A. Widdowson, *J. Chem. Soc., Chem. Commun.*, 1976, 755.
17 N. Ono, R. Tamura and A. Kaji, *J. Am. Chem. Soc.*, 1983, **105**, 4017.
18 N. Ono and A. Kaji, *Synthesis*, 1986, 693 (review); N. Ono, R. Tamura and A. Kaji, *J. Am. Chem. Soc.*, 1983, **105**, 4017; 1980, **102**, 2851.
19 T. A. B. M. Bolsman, J. W. Verhoeven and Th. J. de Boer, *Tetrahedron*, 1975, **31**, 1015; T. A. B. M. Bolsman and Th. J. de Boer, *Tetrahedron*, 1975, **31**, 1023.
20 D. P. Curran and D. Kim, *Tetrahedron*, 1991, **47**, 6171; D. P. Curran, D. Kim and C. Ziegler, *Tetrahedron*, 1991, **47**, 6189; D. P. Curran and G. Thoma, *J. Am. Chem. Soc.*, 1992, **114**, 4436; D. P. Curran and C. M. Seong, *Tetrahedron*, 1992, **48**, 2157.
21 D. P. Curran and C.-T. Chang, *Tetrahedron Lett.*, 1987, **28**, 2477.
22 E. C. Ashby and T. N. Pham, *Tetrahedron Lett.*, 1984, **25**, 4333.
23 J. Hirsch, in *Topics in Stereochemistry*, eds. N. L. Allinger and E. L. Eliel, Wiley-Interscience, New York, 1967, vol. 1, pp. 199–222; P. A. Wade, W. P. Dailey and P. J. Carroll, *J. Am. Chem. Soc.*, 1987, **109**, 5452.
24 T. A. B. M. Bolsman and Th. J. de Boer, *Tetrahedron*, 1973, **29**, 3579.
25 A. H. Pagano and H. Schechter, *J. Org. Chem.*, 1970, **35**, 295; H. Schechter and R. B. Kapan, *J. Am. Chem. Soc.*, 1953, **75**, 3980; R. B. Kaplan and H. Schechter, *J. Am. Chem. Soc.*, 1961, **83**, 3335.
26 P. A. Wade, W. P. Dailey and P. J. Carroll, *J. Am. Chem. Soc.*, 1987, **109**, 5452; G. Rosini, E. Marotta and M. Petrini, *Synthesis*, 1986, 237.
27 G. Descotes, Y. Bahurel, M. Bourillot, G. Pingeon and R. Rostaing, *Bull. Soc. Chim. Fr.*, 1970, 282.
28 W. E. Noland, B. A. Langager, J. W. Manthey, A. G. Zacchei, D. L. Petrak and G. L. Eian, *Can. J. Chem.*, 1967, **45**, 2969.
29 D. Mauzerall and F. H. Westheimer, *J. Am. Chem. Soc.*, 1955, **77**, 2261.
30 S. Kambe and H. Yasuda, *Bull. Chem. Soc. Jpn.*, 1968, **41**, 1444.
31 J. Melton and J. E. McMurry, *J. Org. Chem.*, 1975, **40**, 2138.
32 A. Bhattacharjya, R. Mukhopadhyay and S. C. Prakashi, *Synthesis*, 1985, 886.
33 W. R. Bowman and G. D. Richardson, *J. Chem. Soc., Perkin Trans. 1*, 1981, **22**, 1551.
34 E. M. Sheldrick, 1976, SHELX76. Program for crystal structure determination, University of Cambridge, England, as implemented at the University of Manchester regional computer centre and at Loughborough University of Technology. Scattering factors were taken from the program.

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