Oxidative Addition Reactions of ω-Alkenyl Nitronate Anions

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Anions are oxidatively added to nitronate anions to yield α-substituted nitroalkanes when potassium hexacyanoferrate(III) is used as oxidant. Oxidation of nitronate anions yields intermediate α-nitroalkyl radicals, which undergo addition by anions to give intermediate α-substituted nitroalkane radical anions, which are further oxidised to yield the α-substituted nitroalkanes. The nitronate anions used are derived from 5-nitrohex-1-ene, 6-nitrohept-1-ene, *endo*-5-nitro-*exo*-6-phenylbicyclo[2.2.1]-hept-2-ene, and 1-(bicyclo[2.2.1]hept-5-en-*endo*-2-yl)-2-nitropropane. The intermediate α-nitroalkyl radicals underwent addition of anions to form radical anions faster than intramolecular cyclisation onto the ω-alkenes. The α-nitroalkyl radical derived from 1-(bicyclo[2.2.1]hept-5-en-*endo*-2-yl)-2-nitropropane underwent cyclisation when the oxidation was carried out in the absence of an added anion. The addition of anions (thiocyanate, benzenesulfinate, 4-chlorobenzenethiolate, and nitrite) to the α-nitroalkyl radicals derived from *endo*-5-nitro-*exo*-6-phenylbicyclo[2.2.1]hept-2-ene occurred stereoselectively from the less hindered *exo* face. Oxidative addition of 4-chlorobenzenethiolate to the nitronate from *endo*-5-nitro-*exo*-6-phenylbicyclo[2.2.1]hept-2-ene gave an unusual cyclisation *via* addition of a thiyl radical to the alkene.

The oxidative addition of various anions to nitronate anions is now a well established method for the synthesis α-substituted nitroalkanes.[1] The general mechanism for the oxidative addition reaction is shown in Scheme 1. The initially developed

$$R_2C{=}NO_2^- + Fe^{III} \longrightarrow R_2\dot{C}{-}NO_2 + Fe^{II}$$
$$R_2\dot{C}{-}NO_2 + A^- \longrightarrow [R_2C(A)NO_2]^{\bullet -}$$
$$[R_2C(A)NO_2]^{\bullet -} + Fe^{III} \longrightarrow R_2C(A)NO_2 + Fe^{II}$$
$$\text{Summary: } R_2C{=}NO_2^- + A^- \longrightarrow R_2C(A)NO_2 + 2e^-$$

Scheme 1 Mechanism of oxidative addition of anions to nitronate anions

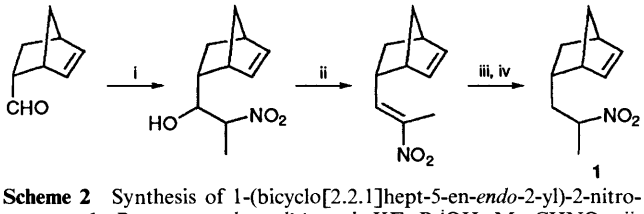
method included addition of nitrite, benzenesulfinate, cyanide, and nitronate anions.[1,2] Other anions now also include thiolates,[3] azides,[4] thiocyanates,[5] *N*-anions of nitrodiazoles,[6] *N*-heterocyclic thiolates[7] and hydroxide.[8] Oxidative cyclisation of anions onto nitronates has also proved to be successful, *e.g.* cyclisation of β-hydroxy nitronates to yield α-nitrooxiranes,[8] cyclisation of phenolates *via* the *para* position,[9] and cyclisation of nitronates to yield vicinal dinitrocyclopropanes,[10] -cyclobutanes[11] and -cyclopentanes.[12] These reactions indicate that the addition of various nucleophiles to intermediate α-nitroalkyl radicals is a favourable process. The use of oxidants other than potassium hexacyanoferrate (III) have been less successful and the nitronate is often oxidised to the corresponding ketone.[2]

The cyclisation of alkenes onto a wide variety of radicals, especially carbon-centred radicals, has become a central synthetic methodology.[13] However, the use of α-nitroalkyl radicals had not been previously studied and, therefore, one of the aims of this work was to develop the cyclisation of alkenes onto intermediate α-nitroalkyl radicals as a general synthetic method. A number of different methods for generating the intermediate α-nitroalkyl radicals were investigated in attempts to facilitate the cyclisations. One of these, the reduction of alkenyl α-halogenonitroalkanes with tributyltin hydride, has already been reported[14] but the success was limited. During the initial part of our project similar studies were reported,[15] also with no success. This paper reports our studies towards the cyclisation of intermediate alkenyl α-nitroalkyl radicals, generated by means of the oxidative addition methodology. A future paper[16] will report the generation of alkenyl α-nitroalkyl radicals using $S_{RN}1$ reactions, reduction of α-halogenonitroalkanes with dihydrobenzylnicotinamide, and photolysis of α-iodonitroalkanes.

Results and Discussion

Synthesis of Alkenyl Nitroalkanes.—Synthesis of 5-nitrohex-1-ene was carried out by standard procedures. Hex-5-en-2-one was reduced to hex-5-en-2-ol with sodium borohydride. Bromination with phosphorus tribromide gave poor yields and therefore the mesyl derivative was prepared. Treatment of the mesyl ester with lithium bromide in acetone[17] or tetrahydrofuran (THF)[18] gave a good yield of the bromide. Use of the tosyl derivative gave only a 22% yield of the bromide. Treatment of 5-bromohex-1-ene with sodium nitrite in dimethylformamide (DMF) gave a 25% yield of 5-nitrohex-1-ene and a by-product, hex-5-en-2-yl nitrite (~20%). 6-Nitrohept-1-ene was prepared by addition of but-3-enylmagnesium bromide to 2-nitropropene.[16] *endo*-5-Nitro-*exo*-6-phenylbicyclo[2.2.1]-hept-2-ene was prepared by the literature method[19] *via* Diels–Alder addition of β-nitrostyrene to cyclopentadiene which gave a mixture of two diastereoisomers in the ratio 83:17. The required product was the major isomer and was separated by chromatography.

1-(Bicyclo[2.2.1]hept-5-en-*endo*-2-yl)-2-nitropropane **1** was prepared from bicyclo[2.2.1]hept-5-ene-2-carbaldehyde by using a Henry reaction,[12,20] dehydration of the resulting hydroxy nitro compound,[12,21] and reduction of the resulting nitroalkene with sodium borohydride[12,22] as shown in Scheme 2.



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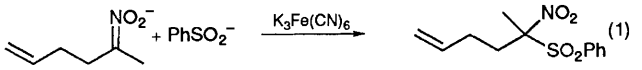
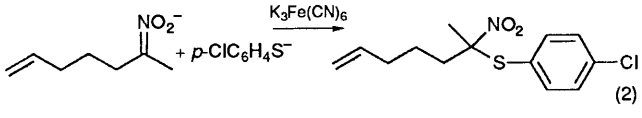
Scheme 2 Synthesis of 1-(bicyclo[2.2.1]hept-5-en-*endo*-2-yl)-2-nitropropane **1**. *Reagents and conditions:* i, KF, Pr^iOH, Me_2CHNO_2; ii, MsCl, Et_3N, CH_2Cl_2; iii, $NaBH_4$; iv, $H_2NOH{\cdot}HCl$.

Oxidative Addition to Acyclic Alkenyl Nitronate Anions.—Simple alkenyl nitronate anions (*e.g.*, the nitronate anions

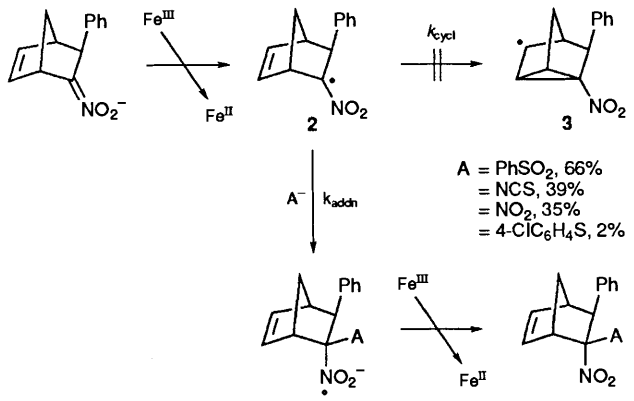
derived from 5-nitrohex-1-ene and 6-nitrohept-1-ene) were initially used with anions known to undergo oxidative additions (*e.g.*, benzenesulfinate and 4-chlorobenzenethiolate anions). A sample reaction with each gave good yields of the product of oxidative addition but not traces of any cyclised material. The reaction between the nitronate anion of 5-nitrohex-1-ene and benzenesulfinate gave 5-nitro-5-phenylsulfonylhex-1-ene in 33% yield [equation (1)] and the corresponding ketone, hex-5-en-2-one (7%). Although cyclisation to a five-membered ring would have to be *via* an *endo* radical, there is evidence[14] that indicates that the cyclisation of this alkenyl α-nitroalkyl takes place *via* reaction between the *O*-centre of the radical to yield an *exo* radical intermediate, which rearranges to a cyclopentane derivative. The reaction between the nitronate anion of 6-nitrohept-1-ene and 4-chlorobenzenethiolate anion gave the expected product of oxidative addition, 6-(4-chlorophenylthio)-6-nitrohept-1-ene (42%) [equation (2)] and the corresponding disulfide (57%). The result indicates that oxidation of the thiolate to thiyl radicals may be faster than oxidation of the nitronate anion to α-nitroalkyl radicals. Addition of thiyl radicals to the nitronate anion would yield the same product as addition of α-nitroalkyl radicals to thiolate anions. The disulfide results from addition of thiyl radicals to thiolate to yield the disulfide radical anion $[(RS–SR)^{\bullet -}]$ which will readily undergo oxidation to yield the disulfide.





Oxidative Addition Reactions of the Nitronate Anion from endo-5-*Nitro*-exo-6-*phenylbicyclo*[2.2.1]*hept*-2-*ene*.—The bicyclo[2.2.1]hept-2-enyl system was chosen as a precursor which would be likely to exhibit cyclisation reactions because of the well known ability[23] of this system to undergo radical cyclisation, and the buttressing effect of the *exo*-6-phenyl substituent should also help facilitate cyclisation. Although cyclisation to a three-membered ring is not normally favourable, the buttressing effects and orientation of molecular orbitals (MOs) in the bicyclo[2.2.1]hept-2-enyl system allow cyclisation to take place. The results of the oxidative addition reactions are shown in Scheme 3. Benzenesulfinate, thiocyanate, and nitrite gave good yields of the expected α-substituted nitro compounds but no traces of cyclised materials. Again, the rate of addition of the anions to the intermediate α-nitroalkyl radicals **2** was faster than cyclisation to the intermediate radical **3** ($k_{addn} \gg k_{cycl}$). Cyanide gave an intractable mixture of products in which hydrolysis of the cyanide to the primary amide appeared to be taking place.

The addition of nucleophiles to the intermediate α-nitroalkyl radicals **2** takes place stereoselectively from the less hindered *exo* face. This is the first example of stereoselectivity in the addition of anions to α-nitroalkyl radicals which are in a chiral environment. A previous example of stereoselective addition of anions to intermediate *p*-nitrobenzylic radicals (in a chiral molecule) to form radical anions has been reported.[24] Similar stereoselective formation of radical anions has also been reported for the addition of *p*-nitrobenzyl radicals to nitronate anions present in chiral molecules.[24] The result is not unexpected as *exo* attack onto bicyclo[2.2.1]heptanes is well



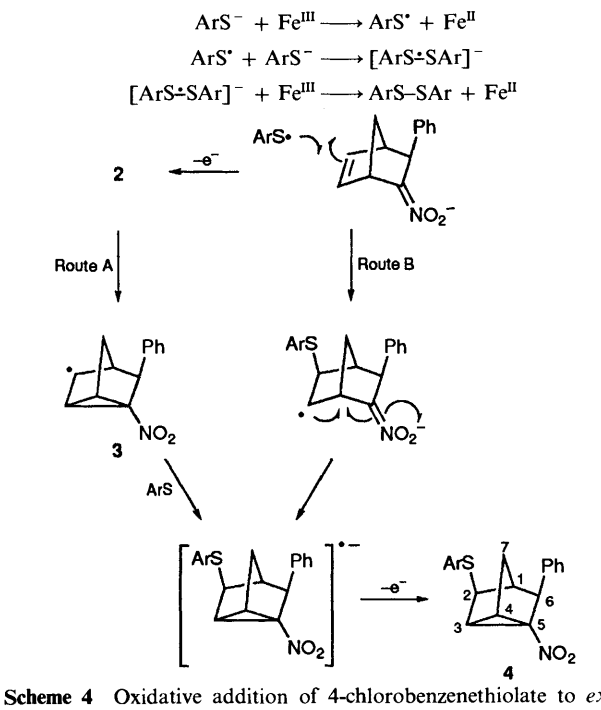
Scheme 3 Oxidative addition of anions to *exo*-3-phenylbicyclo[2.2.1]-hept-5-en-2-nitronate

established. The results do suggest that addition of anions to the intermediate radicals is under kinetic control, *i.e.* the product results from the fastest nucleophile attack (*exo* ≫ *endo*). We have previously shown[1,6] that the addition of anions to 2-nitropropan-2-yl radicals ($Me_2\dot{C}NO_2$) is under kinetic and not thermodynamic control because the stability of the radical anion is not achieved until well past the transition state. The stability of the radical anion $[Me_2C(A)NO_2]^{\bullet -}$ is a function of the π* MO of the nitro group which is only achieved after relaxation and rearrangement of the MOs from the higher energy σ* radical anion $[Me_2C(NO_2)–{}^{\bullet}A]^-$ in which the unpaired electron resides in the σ* MO. The transition state will precede this σ* radical anion and not the lower energy π* radical anion.

The oxidative reaction using 4-chlorobenzenethiolate also results in the corresponding disulfide (21%) and a cyclised, tricyclic nitro compound **4** (10% after extensive purification). This formation of this product suggests that the intermediate α-nitroalkyl radical **2** cyclises to the radical **3**, which then undergoes attack by thiolate (Route A in Scheme 4). However, we suggest that the large amount of disulfide produced indicates that thiyl radicals are initially formed which add to the double bond of *exo*-3-phenylbicyclo[2.2.1]hept-5-en-2-nitronate as shown in Route B in Scheme 4. A precedent is reported in the literature[23] in which thiyl radicals add to the 5-position of bicyclo[2.2.1]hept-5-en-2-one. The resulting radical undergoes cyclisation onto the 2-ketone to yield intermediate cyclopropylalkoxyl radicals.

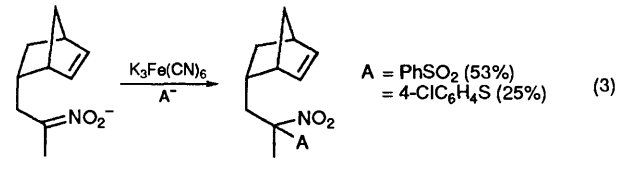
In an attempt to force cyclisation of the intermediate radical **2**, the reaction was carried out in an absence of an added nucleophile. We reasoned that addition of *exo*-3-phenylbicyclo-[2.2.1]hept-5-en-2-nitronate to radical **2** would be sterically hindered. Nitronate anions are strongly solvated in protic solvents and will therefore be unreactive as nucleophiles. The low reactivity of nitronates[1,25] in radical–radical-anion reactions has been clearly demonstrated. Both these factors should slow the addition reaction and favour cyclisation. However, the reaction gave *endo*-5-nitro-*exo*-6-phenylbicyclo[2,2,1]hept-2-ene (78%) and no other major products. The most likely explanation is that abstraction of hydrogen from dichloromethane (CH_2Cl_2) by the α-nitroalkyl radical **2** is faster than cyclisation. A repeat reaction carried out with tetrachloromethane did not appear to give the α-chloronitro analogue but instead gave an intractable mixture of products. Surprisingly neither reaction gave any *exo*-3-phenylbicyclo[2.2.1]hept-5-en-2-one from rearrangement[14] of radical **2**.

Oxidative Addition Reactions of the Nitronate Anion from 1-(*Bicyclo*[2.2.1]*hept*-5-*en*-endo-2-*yl*)-2-*nitropropane*.—This system was chosen because it is the nitro analogue of the 2-



Scheme 4 Oxidative addition of 4-chlorobenzenethiolate to *exo*-3-phenylbicyclo[2.2.1]hept-5-en-2-nitronate

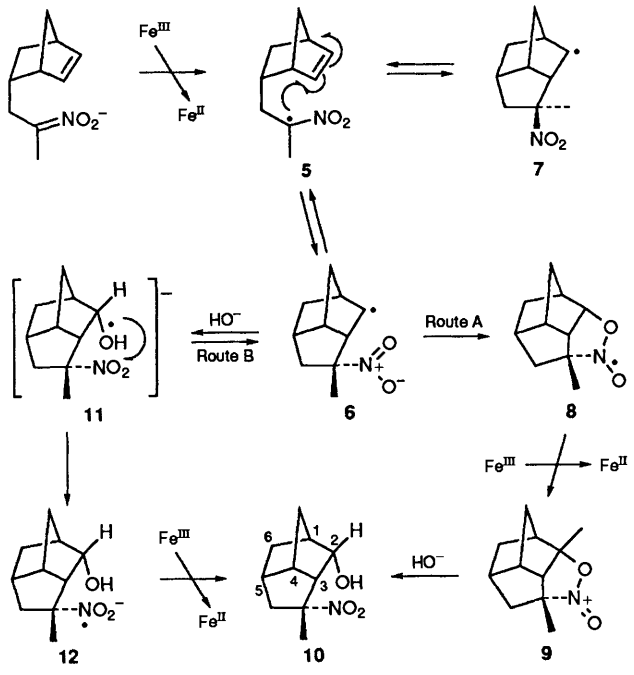
(bicyclo[2.2.1]hept-5-en-*endo*-2-yl)ethyl radical which has been reported[26] to cyclise extremely rapidly with a rate of ~ 1 × 10^7 s^{-1} at 65 °C. Therefore, cyclisation should be observed if at all feasible under the conditions of oxidative addition. Disappointingly the reactions with benzenesulfinate and 4-chlorobenzenethiolate gave addition without any cyclisation [equation (3)]. The thiolate reaction also yielded a large amount of disulfide and 1-(bicyclo[2.2.1]hept-5-en-*endo*-2-yl)propan-2-one (24%). The ketone is probably formed by rearrangement of the intermediate α-nitroalkyl radical **5**[14,27] but appears to be formed in only the thiolate oxidative reactions.



A = $PhSO_2$ (53%)
= 4-ClC_6H_4S (25%) (3)

In order to improve the chance of cyclisation of 1-(bicyclo[2.2.1]hept-5-en-*endo*-2-yl)-2-nitropropan-2-yl radicals **5**, the nitronate was oxidised in the absence of a nucleophile. An unusual product (**10**) was isolated, which obviously resulted from cyclisation of intermediate radical **5** to species **6** (Scheme 5), *i.e.* the above premise is correct in extreme circumstances. However, the product was not one of the expected dimeric products resulting from dimerisation of radicals **6** or **7**, or oxidative addition of species **5** or **6**/**7** to the starting nitronate.

The stereoselectivity of the reaction is most marked and requires an explanation. If A^--values (free energy differences) are a useful guide for this system, the difference between methyl (1.7) and nitro (1.1)[10,28] is not sufficiently large to explain the stereoselectivity. Two possible mechanisms are shown in Scheme 5. The only precedent is the hydroxylation of the cumylic carbon in a reaction proceeding *via* reaction of the *o*-nitrocumyl radical with an oxygen atom of the *ortho*-nitro group.[29] Both mechanisms require a reversible cyclisation of radical **5** to tricyclic species **6** or **7** and the 'fixing' of the nitro group in the *endo* position. Route A invokes a tandem cyclisation in which the unpaired electron of C-2 reacts with the oxygen of the nitro group to form a nitroxyl radical **8**. Nitroxyls are stable, thereby acting as a driving force for this reaction, and are easily oxidised. The cation **9**, resulting from oxidation, should be readily hydrolysed to yield the isolated compound **10**. When the reaction was repeated with two mole equivalents of added hydroxide, the yield of product **10** rose to 37%. In Route B the addition of hydroxide to radical **6**, to yield the unstable σ* radical anion **11** is proposed. The SOMO energy of the σ* unpaired electron in the 3-electron C–O bond is high and not favoured, but very rapid intramolecular single-electron transfer (SET) to the nitro group is favoured because of the orientation of the groups as shown by the X-ray crystallographic data. The SET would be essentially irreversible and hence act as a driving force for the reaction. SET from the product of addition of hydroxide to the *exo*-nitro radical **7** would not be favoured. Methoxide could also be predicted to react *via* Route B but is perhaps disfavoured because of steric reasons.



Scheme 5 Cyclisation of 1-(bicyclo[2.2.1]hept-5-en-*endo*-2-yl)-2-nitropropan-2-yl radicals

Structure Determination of Tricyclic Nitro Alcohol **10**.—The structure of compound **10** was deduced from the combustion analysis, IR spectrum (ν_{max} 3556 cm^{-1} for OH), and ^1H and ^{13}C NMR spectra [δ_H 4.45 (dd, C*H*OH); δ_C 71.29 (CHOH) and 92.10 (tertiary CNO_2)]. The stereochemistry was determined and the structure confirmed by X-ray crystallography. In order to avoid steric interaction between the hydroxy and nitro groups, these moieties are distorted away from each other as evidenced by the O(1)–C(1)–C(6) and C(1)–C(6)–C(9) bond angles.* The O(1)···O(2) and O(1)···N(1) intramolecular distances show weak interaction with contact between 2.967(4) and 2.748(4) Å, respectively. The molecular structure with X-ray atom-numbering scheme is shown in Fig. 1.

Conclusions.—The failure of alkenyl α-nitroalkyl radicals to cyclise except under biased conditions was unexpected[14,15] and we propose that the reason is that competing reactions are faster due to the strongly electrophilic nature of α-nitroalkyl radicals.

* Tables of bond lengths, bond angles, and atomic coordinates have been deposited at the Cambridge Crystallographic Data Centre. See *Instructions for Authors*, in the January issue.

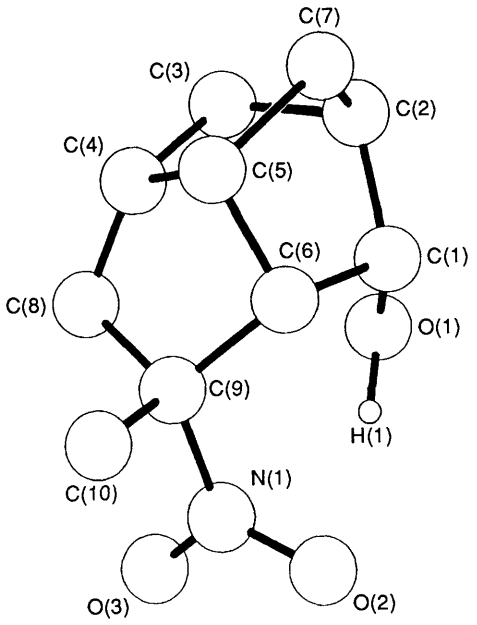


Fig. 1 Molecular structure of tricyclic nitro alcohol **10** with atom-numbering scheme

When α-nitroalkyl radicals are generated from alkenyl α-halogenonitroalkanes using $Bu_3Sn^{\bullet}$ radicals, they are rapidly intercepted by Bu_3SnH, which is a strongly nucleophilic source of hydrogen, *i.e.* the rate of hydrogen abstraction ≫ the rate of cyclisation. Similarly, in the oxidative additions, the rate of anion addition ≫ the rate of cyclisation. When the intermediate α-nitroalkyl radical is attacked intramolecularly by a more nucleophilic group than an alkene then cyclisation appears to be rapid.[8–12] This proposal is supported by the report[30] that enamines (*i.e.*, nucleophilic alkenes) add rapidly to α-nitroalkyl radicals. Therefore, it appears that the cyclisation of α-nitroalkyl radicals for synthetic purposes will only be useful if groups more nucleophilic than unactivated alkenes are present.

Lastly, a possible explanation for the lack of cyclisation is that α-nitroalkyl radicals are particularly stable, *i.e.* cyclisation is thermodynamically unfavourable. However, a number of reports indicate that α-nitroalkyl radicals are not particularly well stabilised by the nitro group. The electron paramagnetic resonance (EPR) spectra of 2-nitropropan-2-yl radicals do not indicate a large overlap of the unpaired electron into the nitro group, and so the spin density resides largely on the carbon atom.[31] Likewise, the use of resonance stabilisation energy calculations[32] indicates that the nitro group is less stabilising than a methyl group, and the SOMO wave function shows that most of the spin density is on the carbon atom of the radical. Earlier MO calculations on the nitromethyl radical come to the same conclusions.[33]

Experimental

General.—^{1}H NMR spectra were measured using a Varian EM360 spectrometer at 360 MHz and a Perkin-Elmer R32 at 90 MHz, and ^{13}C NMR spectra were measured using a Bruker WP-80 spectrometer at 20.1 MHz. 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 was used as an internal standard 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 were recorded for neat films unless otherwise stated. 2D Chemical-shift (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 boiling range 40–60 °C fraction.

Anhydrous magnesium sulfate was used for the drying of extraction solvents. Deoxygenation of reaction mixtures was achieved by purging them with dry nitrogen for 1 h prior to initiation of reaction. Combustion analyses were performed by the Microanalytical Department of Manchester University.

5-Nitrohex-1-ene.—(a) *5-Mesyloxyhex-1-ene* (*Hex-5-en-2-yl methanesulfonate*). Hex-5-en-2-one was reduced with sodium borohydride to yield hex-5-en-2-ol in 89% yield. Hex-5-en-2-ol (1 g, 0.01 mol) was dissolved in dry pyridine (10 cm^3) and treated at 0 °C with methanesulfonyl chloride (2.34 g, 0.02 moles). The reaction mixture was warmed to room temperature, stirred for 1 h, and poured onto ice. The mixture was carefully acidified to pH 5 with conc. hydrochloric acid and extracted with diethyl ether. The organic fractions were combined, washed with water, dried, filtered, and evaporated to dryness to yield the mesyl ester as an oil (1.55 g, 87%); ν_{max}/cm^{-1} 1640, 1420 and 1180; δ_H 1.40 (3 H, d, *J* 5), 1.62 (2 H, m), 2.05 (2 H, m), 2.95 (3 H, s), 4.85–5.20 (3 H, m) and 5.70 (1 H, m).

(b) *5-Bromohex-1-ene.* 5-Mesyloxyhex-1-ene (15 g, 0.084 mol and lithium bromide (22 g, 3 mol equiv.) were added to dry THF (200 cm^3) and the mixture was refluxed for 6 h (monitored by TLC). The reaction mixture was cooled, poured onto water, and extracted with diethyl ether. The organic fractions were combined, dried, filtered, and evaporated to dryness to give an oil (10.2 g). Flash sinter chromatography gave 5-bromohex-1-ene as a lachrymatory oil (7.6 g, 55%); ν_{max}/cm^{-1} 1635; δ_H 1.68 (3 H, d, *J* 6.5), 2.00 (4 H, m), 4.11 (1 H, m), 4.95 (2 H, m) and 5.60 (1 H, m).

(c) *5-Nitrohex-1-ene.* 5-Bromohex-1-ene (1 g, 6.1 mmol) was dissolved in dry DMF (10 cm^3), and urea (950 mg) and sodium nitrite (631 mg, 1.5 mol equiv.) were added. The mixture was stirred for 48 h (monitored by TLC) at room temperature, poured onto water, and extracted with diethyl ether. The organic fractions were combined, washed with water, dried, filtered, and evaporated to dryness to give a crude oil (1.2 g). Column chromatography gave 5-nitrohex-1-ene as an oil (0.2 g, 25%); b.p. 50 °C at 1.5 mmHg; ν_{max}/cm^{-1} 1640, 1550 and 1360; δ_H 1.52 (3 H, d, *J* 6.5), 2.05 (4 H, m), 4.53 (1 H, m), 4.95 (2 H, m) and 5.60 (1 H, m).

The preparation of 6-nitrohept-1-ene will be reported shortly.[16]

endo-5-*Nitro*-exo-6-*phenylbicyclo*[2.2.1]*hept*-2-*ene.*—Dicyclopentadiene was distilled through a Vigreaux column and cyclopentadiene (b.p. 40 °C/760 mmHg) was collected in a cooled receiver. Cyclopentadiene (13.2 g, 0.2 mol) and β-nitrostyrene (14.9 g, 0.1 mol) were allowed to react at 40 °C in the presence of hydroquinone (0.5 g) for 4 h (monitored by TLC). Excess of cyclopentadiene was distilled off and the residue was purified by flash sinter chromatography to yield *endo*-5-nitro-*exo*-6-phenylbicyclo[2.2.1]hept-2-ene as an oil (19.4 g, 90%); ν_{max}/cm^{-1} 3064, 3028, 1632, 1600, 1534 and 1374; δ_H(90 MHz) 1.75 (2 H, br ABq, 7-H_2), 3.10 (1 H, br s, 1-H), 3.40 (1 H, m, 4-H), 3.50 (1 H, m, 6-H), 4.85 (1 H, t, 5-H), 6.00 (1 H, m, 2-H), 6.45 (1 H, m, 3-H) and 7.20 (5 H, m, Ph).

1-(*Bicyclo*[2.2.1]*hept*-5-*en*-endo-2-*yl*)-2-*nitropropane* **1**.—(a) *Henry reaction.* Bicyclo[2.2.1]hept-5-en-*endo*-2-carbaldehyde (1 mol equiv.) and potassium fluoride (0.05 mol equiv.) were stirred in propan-2-ol (3 mol equiv.) at room temperature. 2-Nitropropane (1.2 mol equiv.) was added dropwise and the mixture was stirred for 24 h until reaction was complete as

monitored by TLC. The reaction mixture was poured onto water and extracted with diethyl ether. The organic fractions were combined, dried, and evaporated to dryness. The residue was purifed by flash sinter chromatography to give the Henry adduct, 1-(*bicyclo*[2.2.1]*hept*-5-*en*-endo-2-*yl*)-2-*nitropropan*-1-*ol* (80%) (Found: C, 61.2; H, 7.9; N, 7.4. $C_{10}H_{15}NO_3$ requires C, 60.91; H, 7.61; N, 7.11%); ν_{max}/cm^{-1} 3420, 3040, 1625, 1543 and 1365; δ_H 1.05–2.45 (5 H, m), 1.90 (1.1 H, dm, Me), 2.00 (1.9 H, d, Me), 2.90–3.30 (3 H, m), 3.65 (0.4 H, m, C*H*OH), 3.80 (0.6 H, m, C*H*OH), 4.57 (1 H, m, $CHNO_2$) and 6.15 (2 H, m, olefinic H) [Found: M^+, 197.1057 (0.4%). $C_{10}H_{15}NO_3$ requires M, 197.1052]; *m*/*z* 151 ($M^+ - NO_2$, 0.5%), 133 (18), 115 (0.5), 91 (8) and 66 (100).

(b) *Dehydration of the Henry adduct.* The Henry adduct (1 mol equiv.) was dissolved in CH_2Cl_2 (10 mol equiv.), and methanesulfonyl chloride (1.2 mol equiv.) was added. The mixture was cooled to 0 °C and triethylamine (3 mol equiv.) was added dropwise to the vigorously stirred mixture. Approximately halfway throuth 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, and the extracts were washed successively with aq. sodium hydrogen carbonate and water, dried, filtered, and evaporated to dryness to yield crude 1-(bicyclo[2.2.1]hept-5-en-*endo*-2-yl)-2-nitropropene (98%); ν_{max}/cm^{-1} 3096, 3060, 1664, 1550 and 1360; δ_H 1.20–2.45 (4 H, m), 2.25 (3 H, s), 3.05 (3 H, m), 6.15 (2 H, m), 6.80 (0.5 H, d) and 7.05 (0.5 H, d).

(c) *Reduction of the nitroalkene.* Sodium borohydride (1.2 mol equiv.) was added in portions to a solution of the nitroalkene (1 mol equiv.) in THF (25 mol equiv.) while the temperature was kept below 60 °C. After the mixture had been stirred for 1 h, water was added and the THF was evaporated off 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, filtered, and evaporated to dryness to give crude title nitroalkane. The residue was purified by flash sinter chromatography to give the alkenyl nitroalkane 1-(*bicyclo*-[2.2.1]*hept*-5-*en*-endo-2-*yl*)-2-*nitropropane* **1** (61%) (Found: C, 61.2; H, 7.9; N, 7.4. $C_{10}H_{15}NO_2$ requires C, 60.9; H, 7.6; N, 7.1%); ν_{max}/cm^{-1} 3056, 1622, 1544 and 1390; δ_H 0.70–3.05 (9 H, m), 1.48 (3 H, d, *J* 6), 4.70 (1 H, m) and 6.05 (2 H, m) [Found: M^+, 181.1094 (0.1%). $C_{10}H_{15}NO_2$ requires M, 181.1102]; *m*/*z* 135 ($M^+ - NO_2$, 2%) and 66 (100).

General Procedure for Oxidative Addition Reactions.—Sodium (1.1 mol equiv.) was dissolved in dry methanol (100 cm^3) and the resulting solution was stirred for 15 min. The nitroalkane (1 mol equiv.) was added in one portion and the mixture was stirred for 30 min. The methanol was evaporated off to dryness and the residue was dissolved in distilled water (50 cm^3). Dichloromethane (50 cm^3) was added and the two-phase mixture was stirred rapidly and treated successively with the appropriate nucleophile (2–4 mol equiv.) in water (10 cm^3) and potassium hexacyanoferrate (III) (2 mol equiv.) in water (10 cm^3). After being stirred for 10 min the organic layer was separated and the aqueous phase was re-extracted with dichloromethane (50 cm^3). The dichloromethane fractions were combined, dried, filtered, and evaporated to yield a crude product, which was further purified as indicated below.

Oxidative addition reaction between sodium hex-5-ene-2-nitronate and sodium benzenesulfinate. 5-Nitrohex-2-ene (235 mg, 1.8 mmol) and sodium benzenesulfinate (450 mg, 2.8 mmol) were allowed to react using the general procedure for oxidative addition. The crude mixture from the reaction was purified by preparative TLC (PLC) to give 5-nitro-5-phenylsulfonylhex-1-*ene* (135 mg, 33%) as a clear yellow gum (Found: C, 53.5; H, 5.6; N, 5.1. $C_{12}H_{15}NO_4S$ requires C, 53.5; H, 5.6; N, 5.2%); ν_{max}/cm^{-1} 1640, 1555, 1340 and 1160; δ_H(90 MHz) 1.90 (3 H, s), 1.95–2.60 (4 H, m), 4.95–5.10 (2 H, m), 5.60 (1 H, m) and 7.65 (5 H, m); *m*/*z* 143 ($M^+ - 126$, 8%), 128 ($M^+ - PhSO_2$, 26), 81 (128 − HNO_2, 38) and 77 (100). PLC also yielded hex-5-en-2-one (12 mg, 7%). The IR spectrum and R_f-value in several solvent systems were identical with those of authentic material.

Oxidative addition reaction between sodium hept-6-ene-2-nitronate and sodium 4-chlorobenzenethiolate. The reaction between 6-nitrohept-1-ene (1.00 g, 6.9 mmol) and sodium 4-chlorobenzenethiolate (3.50 g, 21 mmol) using the general procedure gave a crude reaction mixture. ^{1}H NMR spectroscopy of the crude material indicated the presence of bis-(4-chlorophenyl) disulfide (1.70 g, 57%) and 6-(4-chlorophenylthio)-6-nitrohept-1-ene (0.80 g, 42%). The IR and ^{1}H NMR spectra and m.p. of the disulfide, isolated by recrystallisation, were identical with those of authentic material. Evaporation of the filtrate gave 6-(4-chlorophenylthio)-6-nitrohept-1-ene; ν_{max}/cm^{-1} 3076, 1640, 1540 and 1386; δ_H(60 MHz) 1.15–2.45 (6 H, m), 1.77 (3 H, s), 5.02 (2 H, m), 5.51 (1 H, m) and 7.4 (4 H, br s).

Oxidative addition reactions of sodium exo-3-*phenylbicyclo*-[2.2.1]*hept*-5-*ene*-2-*nitronate.* Sodium *exo*-3-phenylbicyclo-[2.2.1]hept-5-ene-2-nitronate and the respective nucleophiles were allowed to react using the general procedure for oxidative addition.

(a) *Sodium benzenesulfinate.* Recrystallisation of the crude product mixture (1.94 g) from the reaction between *endo*-5-nitro-*exo*-6-phenylbicyclo[2.2.1]hept-2-ene (1.50 g, 7 mmol) and sodium benzenesulfinate (3.45 g, 21 mmol) gave endo-5-*nitro*-exo-6-*phenyl*-exo-5-(*phenylsulfonyl*)*bicyclo*[2.2.1]*hept*-2-*ene* (1.65 g, 66%), m.p. 165–167 °C (from MeOH) (Found: C, 63.9; H, 4.9; N, 3.9. $C_{19}H_{17}NO_4S$ requires C, 64.2; H, 4.8; N, 3.9%); ν_{max}/cm^{-1} 3060, 3028, 1602, 1580, 1540, 1342 and 1150; δ_H 1.97 (1 H, br d, *J* 11, 7-H *anti*), 3.05 (1 H, m, 7-H *syn*), 3.25 (1 H, m, 1-H), 3.75 (1 H, m, 4-H), 3.95 (1 H, m, 6-H), 6.10 (1 H, m, *J* 8, 2-H), 6.70 (1 H, m, *J* 8, 3-H) and 7.40 (10 H, m, Ph); δ_C 47.44 (C-7), 48.20 (C-1), 50.95 (C-4), 54.60 (C-6), 116.90 (C-5), 127.56 and 127.75 (C-2 and -3), 127.51, 127.76, 128.52, 130.22, 130.51, 130.67, 134.44, 135.01, 135.49 and 144.73; [Found: $M^+ - NO_2$, 309.0948 (100%). $C_{19}H_{17}O_2S$ requires M, 309.0811]; *m*/*z* 214 ($M^+ - PhSO_2$, 6%) and 167 [$M^+ - (PhSO_2, H, NO_2)$, 100].

(b) *Sodium nitrite.* Recrystallisation (hexane) of the crude orange solid (565 mg) from the reaction between *endo*-5-nitro-*exo*-6-phenylbicyclo[2.2.1]hept-2-ene (1.0 g, 4.7 mmol) and sodium nitrite (1.3 g, 19 mmol) gave 5,5-*dinitro*-exo-6-*phenylbicyclo*[2.2.1]*hept*-2-*ene* (419 mg, 35%) as platelets, m.p. 115–116 °C (from hexane) (Found: C, 59.6; H, 4.5; N, 10.6. $C_{13}H_{12}N_2O_4$ requires C, 60.0; H, 4.6; N, 10.7%); ν_{max}(Nujol)/cm^{-1} 3020, 1638, 1602, 1560 and 1362; δ_H 2.24 (1 H, d, *J* 10, 7-H *anti*), 2.95 (1 H, d, *J* 10, 7-H *syn*), 3.35 (1 H, br s, 1-H), 3.80 (1 H, m, 4-H), 4.32 (1 H, d, *J* 3.5, 6-H), 6.00 (1 H, m, *J* 8, 2-H), 6.68 (1 H, m, *J* 8, 3-H) and 7.20 (5 H, br s, Ph) [Found: $M^+ - NO_2$, 214.0881 (14%). $C_{13}H_{12}NO_2$ requires M 214.2433]; *m*/*z* 260 (M^+, 0.1%) and 167 ($M^+ - NO_2 - HNO_2$, 100).

(c) *Sodium thiocyanate.* Recrystallisation (MeOH) of the crude orange solid (900 mg) from the reaction between *endo*-5-nitro-*exo*-6-phenylbicyclo[2.2.1]hept-2-ene (1.5 g, 7 mmol) and sodium thiocyanate (2.4 g, 25 mmol) gave endo-5-*nitro*-exo-6-*phenyl*-exo-5-*thiocyanatobicyclo*[2.2.1]*hept*-2-*ene* (700 mg, 39%) as plates, m.p. 107–108 °C (Found: C, 62.1; H, 4.45; N, 10.1. $C_{14}H_{12}N_2O_2O_2S$ requires C, 61.8; H, 4.4; N, 10.3%); ν_{max}(Nujol)/cm^{-1} 3076, 1674, 1544 and 1348; δ_H(90 MHz) 2.10 (1 H, br d, *J* 11, 7-H *anti*), 2.50 (1 H, br d, *J* 11, 7-H *syn*), 3.30 (1 H, br s, 1-H), 3.88 (1 H, dd, *J* 3.5, 6-H), 3.95 (1 H, br, 4-H), 6.08 (1 H, dd, *J* 8 and 3.5, 2-H), 6.60 (1 H, dd, *J* 8 and 3.5, 3-H) and 7.30 (5 H, br s, Ph) [Found: $M^+ - NO_2$, 226.0691 (8%).

$C_{14}H_{12}NS$ requires M 226.0690]; *m/z* 167 (83%) and 66 (100).

(d) *Sodium 4-chlorobenzenethiolate.* Purification of the crude residue (1.65 g), by flash sinter chromatography, from the reaction between *endo*-5-nitro-*exo*-6-phenylbicyclo[2.2.1]hept-2-ene (1.5 g, 7 mmol) and sodium 4-chlorobenzenethiolate (3.5 g, 21 mmol) gave bis-(4-chlorophenyl) disulfide (1.24 g, 21%). The ^{1}H NMR spectroscopic data and m.p. were identical with those of authentic material. The second fraction was exo-5-(4-*chlorophenylthio*)-endo-5-*nitro*-exo-6-*phenylbicyclo*[2.2.1]*hept-2-ene* (41 mg, 2%), m.p. 129–131 °C (from MeOH) (Found: C, 64.1; H, 4.7; N, 3.9. $C_{19}H_{16}ClNO_2S$ requires C, 63.8; H, 4.5; N, 3.9%); ν_{max}(Nujol)/cm^{-1} 3084, 1666, 1572, 1530 and 1348; δ_H 1.90 (1 H, br d, *J* 11, 7-H *anti*), 2.60 (1 H, d, *J* 11, 7-H *syn*), 3.20 (2 H, br s, 1- and 4-H), 3.77 (1 H, d, *J* 3.5, 6-H), 5.95 (1 H, br dd, *J* 8, 2-H), 6.50 (1 H, br dd, *J* 8, 3-H) and 7.35 (9 H, m, ArH) [Found: M$^+$, 359.0389 (0.3%) and 357.0527 (0.5%); M$^+$ − NO_2 313.0563 (5%) and 311.0644 (13%). $C_{19}H_{16}ClNO_2S$ requires M, 359.0561 and 357.0590; M − NO_2, 313.0632 and 311.0661]; *m/z* 167 (19%) and 118 (100). The third fraction yielded the *tricyclic compound* **4** (Ar = 4-ClC_6H_4) (228 mg, 10%); m.p. 140–142 °C (from MeOH) (Found: C, 63.4; H, 4.8; N, 3.9. $C_{19}H_{16}ClNO_2S$ requires C, 63.8; H, 4.5; 3.9%); ν_{max}(Nujol)/cm^{-1} 1514 and 1370; δ_H(360 MHz) 1.97 (1 H, d, *J* 11.7, 7-H; also coupled to 1- and 4-H), 1.82 (1 H, d, *J* 11.7, 7-H; also coupled to 1- and 4-H), 2.17 (1 H, br s, *J* 0.14, 1-H; also coupled to 7-H_2, 2- and 6-H), 2.72 (1 H, d, *J* 5.8, 3-H; also coupled to 2- and 4-H), 2.80 (1 H, dm, *J* 5.8, 4-H; coupled to 3-H and 7-H_2), 3.18 (1 H, dm, *J* 0.14, 6-H; coupled to 1- and 3-H), 3.66 (1 H, dd, *J* 0.13 and 0.13, 2-H; coupled to 1-and 3-H), 7.10 (2 H, d, *o*-H of C_6H_4S), and 7.23–7.38 (7 H, ArH); δ_C 26.24 (C-4), 27.47 (C-7), 33.58 (C-3), 44.70 (C-1), 50.04 (C-2), 53.31 (C-6), 68.92 (C-5), 127.22, 127.29, 128.54, 129.44, 132.57, 133.20, 133.83, and 135.90; the NMR spectroscopic data were assigned using COSY and ^{1}H–^{13}C correlation techniques [Found: M$^+$, 359.0500 (15%) and 357.0534 (39%). $C_{19}H_{16}ClNO_2S$ requires M, 359.0561 and 357.0590]; *m/z* 167 (M$^+$ − NO_2 − H − SC_6H_4Cl, 100).

Oxidation of sodium exo-3-*phenylbicyclo*[2.2.1]*hept-5-ene-2-nitronate with potassium hexacyanoferrate*(III) *in the absence of a nucleophile.* Sodium *exo*-3-phenylbicyclo[2.2.1]hept-5-ene-2-nitronate (1.0 g, 4.6 mmol) was allowed to react using the general procedure for oxidative addition. ^{1}H NMR spectroscopy indicated *endo*-5-nitro-*exo*-6-phenylbicyclo[2.2.1]hept-2-ene as the only product (78%). Purification of the product by using PLC gave *endo*-5-nitro-*exo*-6-phenylbicyclo[2.2.1]hept-2-ene (390 mg, 39%). A repeat reaction using tetrachloromethane in place of CH_2Cl_2 as solvent gave an intractable mixture.

Oxidative Addition Reactions between Sodium 1-(*Bicyclo*[2.2.1]*hept-5-en*-endo-2-*yl*)*propane-2-nitronate and Nucleophiles.*—(a) *Sodium 4-chlorobenzenethiolate.* 1-(bicyclo[2.2.1]hept-5-en-*endo*-2-yl)-2-nitropropane (1.0 g, 5.5 mmol) and sodium 4-chlorobenzenethiolate (4.1 g, 24.9 mmol) were allowed to react using the general procedure. Analysis of the crude product mixture (1.754 g) by ^{1}H NMR spectroscopy showed the following products and relative yields: bis-(4-chlorophenyl)disulfide (51%), 1-(bicyclo[2.2.1]hept-5-en-*endo*-2-yl)-2-(4-chlorophenylthio)-2-nitropropane (25%), and 1-(bicyclo[2.2.1]hept-5-en-*endo*-2-yl)propan-2-one (24%). Flash sinter chromatography on TLC alumina as absorbent with CH_2Cl_2–light petroleum gave bis-(4-chlorophenyl)disulfide (720 mg). The second fraction was 1-(bicyclo[2.2.1]hept-5-en-*endo*-2-yl)-2-(4-chlorophenylthio)-2-nitropropane as a pale yellow oil (450 mg, 25%); ν_{max}/cm^{-1} 3056, 1644, 1538 and 1386; δ_H 1.45–2.95 (9 H, m), 1.75 (3 H, s, Me), 6.10 (2 H, m, olefinic H) and 7.40 (4 H, m, ArH). Further purification for elemental analysis proved unsuccessful. The third fraction contained 1-(bicyclo[2.2.1]hept-5-en-*endo*-2-yl)propan-2-one (370 mg, 44%), b.p. 75 °C at 1 mmHg; ν_{max}/cm^{-1} 3056, 1712 and 1632; δ_H 1.10–3.30 (7 H, m), 2.10 (3 H, s, Me) and 6.10 (2 H, m, olefinic H).

(b) *Sodium benzenesulfinate.* PLC of the crude product from the reaction between 1-(bicyclo[2.2.1]hept-5-en-*endo*-2-yl)-2-nitropropane (1.0 g, 5.5 mmol) and sodium benzene sulfinate (2.7 g, 17 mmol) gave 1-(*bicyclo*[2.2.1]*hept-5-en*-endo-2-*yl*)-2-*nitro*-2-(*phenylsulfonyl*)*propane* as a pure clear gum (905 mg, 53%) (Found: 59.8; H, 6.2; N, 4.1. $C_{16}H_{19}NO_4S$ requires C, 59.8; H, 5.9; N, 4.3%); ν_{max}/cm^{-1} 3060, 1628, 1582, 1550 and 1332; δ_H(90 MHz) 1.00–2.90 (9 H, m) including 2.00 (3 H, 2 s, diastereotopic Me), 6.10 (2 H, m, olefinic H) and 7.60 (5 H, m, Ph) [Found: M$^+$, 321.1217 (0.02%). $C_{16}H_{19}NO_4S$ requires M, 321.1390]; *m/z* 275 (M$^+$ − NO_2, 0.03%), 209 (2), 183 (6), 180 (5), 141 (7), 125 (12), 109 (11), 77 (38) and 66 (100). No other products were isolated.

Oxidation of Sodium 1-(*Bicyclo*[2.2.1]*hept-5-en*-endo-2-*yl*)-*propane-2-nitronate with Potassium Hexacyanoferrate*(III) *in the Absence of a Nucleophile.*—1-(Bicyclo[2.2.1]hept-5-en-*endo*-2-yl)-2-nitropropane (600 mg, 3.0 mmol) was allowed to react using the general procedure for oxidative addition. Trituration of the crude product (376 mg) with hexane, followed by recrystallisation (hexane), gave the cyclised compound **10** (208 mg, 16%), m.p.: sublimes at 118–125 °C and melts at 140–141 °C (Found: C, 61.4; H, 7.8; N, 7.1. $C_{10}H_{15}NO_3$ requires C, 60.9; H, 7.6; N, 7.1%); ν_{max}/cm^{-1} 3556, 1528 and 1354; δ_H 1.02–3.10 (10 H, m), 1.68 (3 H, s, Me) and 4.45 (1 H, dd, C*H*OH); δ_C 31.11 (Me), 32.69 (C-6), 34.27 (C-5), 34.75 (CH_2CNO_2), 40.94 (C-1), 42.40 (C-7), 46.34 (C-4), 51.50 (C-3), 71.29 (COH) and 91.10 (CNO_2) [Found: M$^+$ − NO_2, 151.1109 (33%). $C_{10}H_{15}O$ requires *m/z*, 151.2279]; *m/z* 197 (M$^+$, 0.1%), 133 (151 − H_2O, 65), 121 (151 − H_2CO, 44) and 93 (100). The structure was confirmed by X-ray crystallography.

Crystal Data for Compound **10**.—$C_{10}H_{15}NO_3$, M = 197.23, monoclinic, *a* = 6.423(10), *b* = 12.245(4), *c* = 12.969(5) Å, β = 110.9(2)°, *V* = 952.81 Å^3 (by optimisation of axial row reflections), space group $P2_1/c$, *Z* = 4, D_x = 1.375 g cm^{-3}, crystal dimensions: 0.87 × 0.14 × 0.12 mm, μ(Mo-Kα) = 0.51 cm^{-1}.

Data Collection and Processing.—Stoe Stadi-2 Weissenberg diffractometer, ω scan, graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å); 1638 reflections ($5 < 2\theta < 50$) of which 1126 were observed with $F/\sigma(F) > 6.0$; standard reflections measured on each layer indicated negligible crystal decay, *T* = 293 K. Data were corrected for Lorentz and polarisation effects but not absorption.

Structure Analysis and Refinement.—The structure was solved by direct methods (SHELX 76) and resolved by full matrix least-squares based on *F* with unit weights. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were located by a difference map with only isotropic temperature factors refined. Final shift/error 0.000. The final *R*-value was 0.041 for 1126 reflections and 142 refined parameters. Electron-density residuals in the final difference map were − 0.2 ⟶ 0.2 e Å^{-3}. Programs and computers used are in ref. 34.*

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* Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre (see *Instructions for Authors*, in the January issue).

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