Nitrobicyclo[2.2.1]heptanes. Part 8.[1] Neighbouring-Group Participation by Nitro Groups during the Reaction of *endo*-Nitrobicyclo[2.2.1]heptenes with Electrophiles

Joseph P. Michael,* Norman F. Blom and Luéta-Ann Glintenkamp
Centre for Molecular Design, Department of Chemistry, University of the Witwatersrand, Wits 2050, South Africa

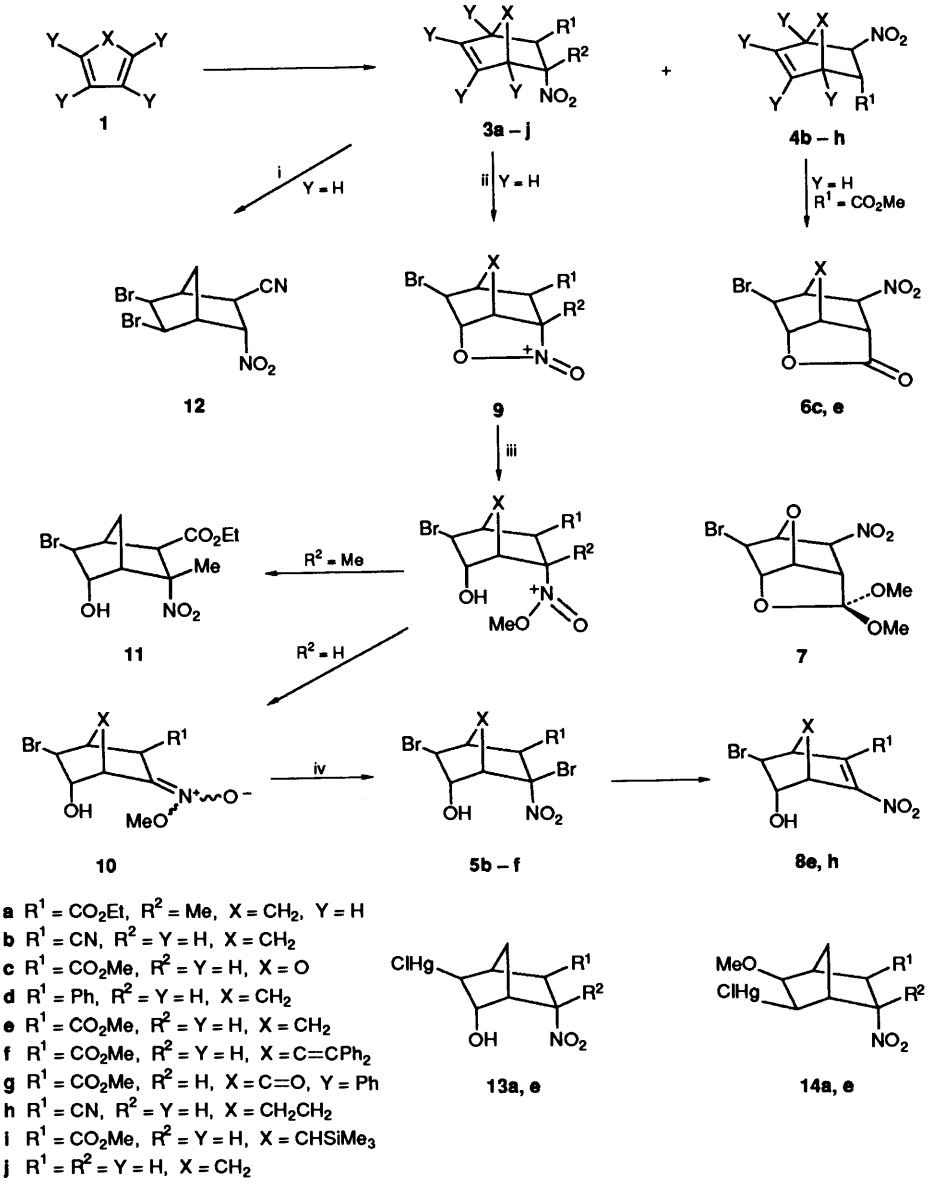
Cyclic dienes **1** undergo Diels–Alder reactions with several nitroalkenes **2** to give adducts in which the *endo*-nitro isomers **3** are the major constituents. These isomers react with *N*-bromosuccinimide in methanol to produce regio- and stereo-selectively functionalised nitrotrinorbornanols **5**, which result from neighbouring-group participation by the nitro group during electrophilic bromination. A mechanistic proposal is presented together with evidence for the intermediacy of nitronate esters **10**, and the scope of the reaction is briefly explored. Reactions of *endo*-nitrotrinorbornenes **3** with mercury(II) trifluoroacetate in methanol give more *cis,exo*-methoxymercuriation product **14** than nitro-group-participation product **13**. An apparently unprecedented ^4J ^{199}Hg–^1H coupling in the former is described.

The bicyclo[2.2.1]heptane, or trinorbornane, system is a touchstone for the study of neighbouring-group effects because of the enforced proximity in which functional groups appended to its skeleton may find themselves. In electrophilically initiated additions to bicyclo[2.2.1]heptenes, for instance, the concave *endo* cavity is usually inaccessible to external reactants; but *endo*-positioned functional groups, already located within this envelope, readily become involved as nucleophilic partners once an external electrophile has initiated reaction at the *exo* face of the C=C bond. Since the participating group transfers an atom or cluster of atoms across the ring system in a fashion determined by geometrical constraints, the outcome is a regiospecific, highly stereoselective functionalisation of the C=C bond. Examples of this process abound, and the participating functional groups and electrophilic initiators can be quite varied. Hydroxyalkyl groups or carboxylic acids and their derivatives are very common nucleophilic partners in neighbouring-group participation.[2] Less familiar participants in trinorbornenyl systems include the alcohol,[3] aminomethyl,[4] *N,O*-bis(trimethylsilyl)imidate,[5] nitrile,[6] sulphoxide[7] and sulphone[8] functionalities. To this list we have added the nitro group. We now give full details of results reported in a prior communication,[9] together with additional examples.

Results and Discussion

The Diels–Alder reaction between cyclic dienes **1** and various nitroalkenes **2** was used to prepare substates **3**, which were accompanied by lesser amounts of their *exo*-nitro stereoisomers **4** (Scheme 1). Subsequent reactions were performed on the isomer mixtures whenever separation proved to be difficult or impossible. Adducts **3a–d**/**4a–d** have been described in the literature.[10–13] The adduct from methyl (*E*)-3-nitropropenoate (**2**; $R^1 = CO_2Me$, $R^2 = H$) and cyclopentadiene has also been reported (43% yield),[14] but without stereochemical assignment. On carrying out the reaction in benzene at 0 °C, we obtained a quantitative yield of products **3e**/**4e** (86:14 by NMR; diagnostic signals are for 3-H, which couples with the adjacent bridgehead hydrogen only if orientated *exo*[15]). Fractional crystallisation from the melt gave a pure sample of the major isomer **3e** for characterisation. By contrast, the new compounds **3f** and **4f**, from diphenylfulvene (**1**; X = C=CPh$_2$, Y = H) and nitroalkene (**2**; $R^1 = CO_2Me$, $R^2 = H$), were easily separated by column chromatography (77 and 18% respectively). From dienophile (**2**; $R^1 = CO_2Me$, $R^2 = H$) and tetraphenylcyclopentadienone (**1**; X = C=O, Y = Ph) was obtained a single adduct, compound **3g** (85%), whose isomer, compound **4g**, could be detected in the mother liquors after recrystallisation. The reaction of cyclohexa-1,3-diene (**1**; X = CH_2CH_2, Y = H) and (*E*)-3-nitropropenenitrile (**2**; $R^1 = CN$, $R^2 = H$) at reflux in diethyl ether gave the inseparable isomers **3h** and **4h** in the ratio 4:1 (82%).

Preliminary studies with nitrile **3b**/**4b** and ester **3e**/**4e** isomer mixtures indicated that no reaction occurred on attempted bromination with *N*-bromosuccinimide (NBS) in the presence of radical initiators. However, starting material was consumed when conditions were adjusted to induce electrophilic bromination. With methanol as solvent, two molar equivalents of NBS were necessary for complete consumption of nitriles **3b**/**4b**. The sole product isolated (56%) was inferred from its spectra to be compound **5b**, and this structure was confirmed by an X-ray diffraction study, the results of which have been reported elsewhere.[9] Analogous products were formed under like conditions from most of the other substrates **3**, and these were accompanied on occasion by products derived from the *exo*-nitro contaminants **4**. Thus, the *ca.* 2:1 adduct mixture **3c**/**4c**[12] from furan (**1**; X = O, Y = H) and methyl (*E*)-3-nitropropenoate (**2**; $R^1 = CO_2Me$, $R^2 = H$) gave dibromo alcohol **5c** (64%), together with varying quantities of the bromo lactone **6c** and the corresponding cyclic orthoester **7**. The adduct mixture **3d**/**4d** (4:1) from cyclopentadiene and β-nitrostyrene (**2**; $R^1 = Ph$, $R^2 = H$)[13] gave product **5d** in 65% yield (81% based on **3d**), while the ester isomer mixture **3e**/**4e** yielded compound **5e** (70%) and a small quantity of bromo lactone **6e**. Diphenylfulvene adduct **3f** gave product **5f** (40%), steric hindrance no doubt being responsible for the failure of the *exo*-ester group itself to participate in bromolactonisation with the substituted 7-methylene substituent. Steric effects must also account for the complete inertness of the nitro(tetraphenyl)trinorbornen-7-one **3g** towards the NBS–methanol reagent. The product isolated from the nitrobicyclo[2.2.2]-octene isomer mixture **3h**/**4h** was the bicyclic nitroalkene **8h** (25%), the reaction probably proceeding through compound **5h** followed by a ready dehydrobromination. {In the case of compound **5e** we were able to show that such an elimination is quite easily accomplished, product **8e** being obtained (63%) at room temperature on treatment with 1,8- diazabicyclo[5.4.0]-undec-7-ene (DBU) in tetrahydrofuran (THF) solution.} Nitro-



a $R^1 = CO_2Et$, $R^2 = Me$, $X = CH_2$, $Y = H$
b $R^1 = CN$, $R^2 = Y = H$, $X = CH_2$
c $R^1 = CO_2Me$, $R^2 = Y = H$, $X = O$
d $R^1 = Ph$, $R^2 = Y = H$, $X = CH_2$
e $R^1 = CO_2Me$, $R^2 = Y = H$, $X = CH_2$
f $R^1 = CO_2Me$, $R^2 = Y = H$, $X = C{=}CPh_2$
g $R^1 = CO_2Me$, $R^2 = H$, $X = C{=}O$, $Y = Ph$
h $R^1 = CN$, $R^2 = Y = H$, $X = CH_2CH_2$
i $R^1 = CO_2Me$, $R^2 = Y = H$, $X = CHSiMe_3$
j $R^1 = R^2 = Y = H$, $X = CH_2$

Scheme 1 *Reagents:* i, Br_2, $CHCl_3$; ii, NBS, MeOH; iii, MeOH; iv, NBS

group participation is a minor pathway in the bromination of the 7-trimethylsilyl compound **3i**, as we have shown elsewhere,[16] while the parent compound 2-*endo*-nitrobicyclo-[2.2.1]heptene **3j**[17] failed to give a recognisable product.

As far as could be judged, the functionalisation of the C=C bond during bromination of compounds **3** was regiospecific and totally stereoselective. The position and *endo* orientation of the hydroxy group in products **5**, in particular, provide compelling evidence for the transfer of an oxygen atom from the nitro group as the reaction progresses. Since the reactions worked equally well when carried out in scrupulously dried methanol, the origin of the OH group cannot be adventitious moisture. A plausible mechanism for the reaction (Scheme 1, **3** ⟶ **9** ⟶ **10** ⟶ **5**) assumes that the nitro group intercepts the cationic species formed when the brominating agent reacts at the exposed *exo* face of the double bond. The labile cyclic nitronium intermediate **9** formed in this process must then undergo methanolysis and deprotonation (formally with succinimide anion) to give a nitronate ester **10**, further bromination and demethylation of which lead to the observed products **5**.

The assumption of neighbouring-group participation by the nitro group is unusual enough to require some comment. Nitro groups rarely behave as nucleophiles unless they are first converted into the corresponding nitronate anions.[18] In apparently unambiguous situations, intermolecular interception of electrophilic species by $-NO_2$ is considerably less common[19,20] than the intramolecular interception proposed in reports of oxygen transfer to electrophilic sites. The effect has been most frequently evoked in certain reactions of *o*-nitrophenyl substrates[21] such as *o*-nitrostyrenes,[22] *o*-nitrophenylcyclopropanes,[22] *o*-nitrophenylalkynes,[23] *o*-nitrophenyloxiranes[24] and *o*-nitrobenzyl halides,[25] and less frequently for nitroalkyl substrates.[26,27] Most importantly, intermediates akin to **9** have even been isolated as salts by treatment of the appropriate *o*-nitrostyrene or *o*-nitrophenylcyclopropane with acid and silver hexafluoroantimonate or tetrafluoroborate.[28] The usual products from the collapse of these intermediates are alkyl *o*-nitrosophenyl ketones.

In the present study, no direct evidence was obtained for the formation of intermediates **9**. A naive attempt to precipitate a hexafluorophosphate salt by repeating the reaction of compound **3b** in the presence of ammonium hexafluorophosphate merely resulted in a noticeably faster reaction. The observation agrees with the known promotion of an ionic pathway for NBS-mediated bromination in the presence of added salts.[29] We

were also never able to isolate nitrosotrinorbornanones from the reactions, although the reaction mixtures invariably turned pale blue within a short time. However, concrete evidence for the proposed mechanism came after bromination of the isomeric ester mixture **3e**/**4e** with one molar equivalent of molecular bromine in dry methanol in the presence of sodium hydrogen carbonate. We obtained, in addition to bromo lactone **6e** (12%), an unstable, colourless, solid whose spectra were consistent with the presence of a nitronate ester (**10**; R^1 = CO_2Me, X = CH_2) (40%). The geometry about the C=N bond is uncertain. Further treatment of this product with NBS in methanol brought about clean conversion into product **5e** (60%). If the position α to NO_2 is blocked with a methyl group, formation of the nitronate ester is prevented; nevertheless, the isolation of product **11** (62%) from substrate **3a**[10] indicates that nitro-group participation must still occur. The course of the participation reaction can be diverted by changing the brominating agent: on bromination of the nitrile isomer mixture **3b**/**4b** with molecular bromine in chloroform, the *cis,exo*-dibromo adduct **12** was isolated in variable but generally poor yield (*ca.* 29%). While *cis*-additions of certain electrophiles to trinorbornenes are not uncommon,[30] *cis*-bromination is unusual.[31] The implication in our case, as in a related example involving sulphone substituents,[8] is that the intermediate **9** formed by participation of the *endo* functional group is intercepted by bromide ion attacking from the *exo* direction.

We have had ambiguous results with electrophilic reagents other than NBS (*e.g.*, benzeneselenenyl bromide, epoxidising agents). However, *N*-chlorosuccinimide gave the expected participation reaction with nitrile **3b**, as we have reported in another context.[32] Also successful was reaction with mercury(II) trifluoroacetate in methanol solution. With the ester substrate **3a**, two products were isolated after work-up with sodium chloride. The participation product **13a** proved to be the minor (14%), while the major product **14a** (48%) formed as the result of well precedented[30] *cis,exo*-methoxymercuriation. Substrate **3e** gave, in similar fashion, participation product **13e** (20%) and the product of solvomercuriation, compound **14e** (71%). In this case, the trifluoroacetate counter-ion is not basic enough to induce the formation of an intermediate nitronate ester similar to **10**, and further reaction α to the nitro group was not observed. The ^1H NMR spectra of the methoxymercuriation products **14** clearly demonstrated the stereochemistry of addition, since signals for hydrogen adjacent to the methoxy and chloromercurio groups showed distinct long-range W-coupling to 7-H and no coupling to the adjacent bridgehead protons 1-H and 4-H.[15] The regiochemistry of addition was more difficult to prove, and nuclear Overhauser and COLOC[33] NMR experiments were inconclusive. However, on recording the spectrum of compound **14e** under a variety of conditions, we noticed that the signal at δ 5.29 for 3-H, the proton adjacent to the nitro group, was consistently flanked by satellites at a distance of *ca.* 34 Hz. The intensities of these satellites made up ~18% of the whole signal cluster. Since the natural abundance of the ^{199}Hg isotope is ~17%, we ascribe the satellites to long-range ^{199}Hg–^1H coupling. If the explanation is correct, the chloromercurio group can only be located on C-5, and the coupling (67.8 Hz) must represent ^4J W-coupling between the nuclei. While ^4J coupling has been observed between ^1H and ^{205}Tl nuclei in similar systems,[34] ours appears to be the first example of ^4J W-interaction between mercury and hydrogen.

In view of our continuing interest in the nitro group as a hydrogen-bond acceptor,[1,32] it is worth pointing out that the ^1H NMR signal for the OH group in all the *endo*-hydroxy compounds **5**, **8** and **13** appears as a doublet coupled to the adjacent *exo*-hydrogen (J 2.4–5.0 Hz). In accord with previous arguments,[32] we take the coupling to reflect intramolecular OH···O_2N hydrogen bonding, which locks the OH group into a conformation in which detectable spin–spin coupling is possible. The observed J-range correlates with H–C–O–H dihedral angles of between 113° and 128°.[35]

Experimental

Routine measurements were on a Kofler micro hot-stage (m.p.), Pye-Unicam SP3-300 or PU 9512 (IR), AEI MS-9 or Varian MAT 212 (MS) and Varian EM-360A, Bruker WP-80 and Bruker AC200 (NMR) spectrometers. Decoupling, distortionless enhancement by polarisation transfer (DEPT) and CH-correlated spectra were routinely used for the complete assignment of NMR signals. J-Values are given in Hz. Unless otherwise stated, ^1H spectra were recorded at 200.13 MHz and ^{13}C spectra at 50.32 MHz. Abbreviations: n = *endo*, x = *exo*, a = *anti* and s = *syn*. TLC was on precoated silica gel plates (Merck F254), and column chromatography was on Merck silica gel (particle size 0.063–0.200 mm) or Merck silica gel (particle size 0.040–0.063 mm) for flash chromatography.[36] Methanol was dried by distillation from magnesium activated by iodine. NBS was recrystallised from water before use.

Methyl 3-*Nitrobicyclo*[2.2.1]*hept*-5-*ene*-2-*carboxylate* **3e**/**4e**.—Freshly cracked cyclopentadiene (0.75 cm^3, *ca.* 610 mg, *ca.* 9.2 mmol) was added in one portion to a stirred solution of methyl (*E*)-3-nitropropenoate (**2**; R^1 = CO_2Me, R^2 = H)[37] (1.21 g, 9.23 mmol) in benzene (45 cm^3) at 0 °C. The mixture was kept at this temperature for 30 min, and then at room temperature for 2 h. Removal of the solvent under reduced pressure gave a pale yellow oil (1.80 g, 99%), shown by NMR spectroscopy to consist of a mixture of *methyl* 3-endo-*nitrobicyclo*[2.2.1]*hept*-5-*ene*-2-exo-*carboxylate* **3e** and methyl 3-*exo*-nitrobicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylate **4e** in the ratio 86:14. On occasion, the isomer mixture partly crystallised on storage, and centrifugation of the semi-solid product gave a fairly pure sample of major adduct **3e**, which was further recrystallised from a melt to give needles, m.p. 29–30 °C (Found: C, 54.5; H, 5.6; N, 7.3. $C_9H_{11}NO_4$ requires C, 54.82; H, 5.62; N, 7.10%); R_f [hexane–ethyl acetate (3:1)] 0.60; ν_{max}(neat liquid)/cm^{-1} 3000, 2960, 1735 (C=O), 1546 and 1380 (NO_2), 1441, 1267, 1252, 1201 and 1180; δ_H($CDCl_3$) 6.49 (1 H, dd, J 5.6 and 3.2, 6-H), 6.09 (1 H, dd, J 5.7 and 2.8, 5-H), 5.42 (1 H, t, J 3.8, 3-H), 3.78 (3 H, s, CO_2Me), 3.63 (1 H, m, 4-H), 3.25 (1 H, m, 1-H), 3.06 (1 H, br t, J *ca.* 3, 2-H; on irradiation at δ 3.25, simplifies to dd, J 3.3 and 2.2), 1.70 (1 H, dm, J *ca.* 9.5, 7s-H) and 1.62 (1 H, dm, J *ca.* 9.5, 7a-H; on irradiation at δ 3.06, simplifies to dt, J 9.5 and 1.6); δ_C($CDCl_3$) 172.4 (C=O), 139.2 (C-6), 133.4 (C-5), 87.5 (C-3), 52.4 (CO_2Me), 48.6 (C-2), 47.5 (C-1), 47.1 (C-4) and 46.0 (C-7).

Assignable signals for minor adduct **4e**: δ_H($CDCl_3$) 6.25 (2 H, m, 5- and 6-H, the former marginally upfield), 4.72 (1 H, ddd, J 3.6, 1.6 and 0.7, 3n-H), 3.71 and 3.70 (4 H, overlapping m and s, 2x-H and CO_2Me), 3.49 (1 H, m, 4-H), 3.35 (1 H, m, 1-H), 1.90 (1 H, dm, J *ca.* 9.4, 7s-H) and *ca.* 1.7 (obscured by signals of major adduct, 7a-H); δ_C($CDCl_3$) 171.3 (C=O), 138.4 (C-6), 134.5 (C-5), 87.4 (C-3), 52.1 (CO_2Me), 50.0 (C-2), 49.9 (C-4), 46.8 (C-7) and 44.8 (C-1).

Methyl 7-*Diphenylmethylene*-3-*nitrobicyclo*[2.2.1]*hept*-5-*ene*-2-*carboxylate* **3f**/**4f**.—A solution of methyl (*E*)-3-nitropropenoate (**2**; R^1 = CO_2Me, R^2 = H) (591 mg, 4.51 mmol) and diphenylfulvene (**1**; X = C=CPh_2, Y = H) (654 mg, 2.8 mmol) in dry diethyl ether (55 cm^3) was kept at 0 °C for 3 h and at room temperature for 12 h. (When the reaction was repeated on larger scales, the mixture was kept at room temperature for a period of days until the intense yellow colour of the fulvene was no longer apparent.) Removal of the solvent under reduced

pressure gave a yellow oil, which was separated by column chromatography on silica gel with hexane–ethyl acetate mixtures as eluent to give *methyl* 7-*diphenylmethylene*-3-endo-*nitrobicyclo*[2.2.1]*hept*-5-*ene*-2-exo-*carboxylate* **3f** (791 mg, 77%) as prisms, m.p. 99.5–102.5 °C (from diisopropyl ether) (Found: C, 72.6; H, 5.4; N, 3.9. $C_{22}H_{19}NO_4$ requires C, 73.12; H, 5.30; N, 3.88%); R_f [hexane–ethyl acetate (6:1)] 0.48; $\nu_{max}(CHCl_3)/cm^{-1}$ 3026 (=CH), 1734 (C=O), 1549 and 1373 (NO_2); $\delta_H(CDCl_3)$ 7.35–7.2 (6 H, m, ArH), 7.15–7.1 (2 H, m, ArH), 7.05–6.97 (2 H, m, ArH), 6.64 (1 H, ddd, *J* 5.9, 3.3 and 0.9, 6-H), 6.29 (1 H, ddd, *J* 6.0, 2.8 and 0.8, 5-H), 5.65 (1 H, dd, *J* 4.2 and 3.4, 3x-H), 4.13 (1 H, m, 4-H), 3.69 (1 H, m, 1-H), 3.61 (3 H, s, CO_2Me) and 3.24 (1 H, dd, *J* 3.4 and 0.5, 2n-H); $\delta_C(CDCl_3)$ 171.1 (C=O), 145.8 (C-7), 139.7 (arom C-1), 138.7 (C-6), 134.4 (C-5), 129.0, 128.9, 128.2 and 127.9 (arom C-2, -3), 127.3 and 127.1 (arom C-4), 126.9 (=*C*Ph_2), 85.3 (C-3), 52.3 (CO_2*Me*), 49.7 (C-2), 48.9 (C-1) and 48.5 (C-4); and *methyl* 7-*diphenylmethylene*-3-exo-*nitrobicyclo*[2.2.1]*hept*-5-*ene*-2-endo-*carboxylate* **4f** as a viscous liquid (187 mg, 18%), R_f [hexane–ethyl acetate (6:1)] 0.38; $\nu_{max}(CHCl_3)/cm^{-1}$ 3032 (=CH), 1734 (C=O), 1551 and 1369 (NO_2); $\delta_H(CDCl_3)$ 7.35–7.22 (6 H, m, ArH), 7.15–7.1 (2 H, m, ArH), 7.0–6.97 (2 H, m, ArH), 6.50 (1 H, ddd, *J* 5.9, 2.8 and 1.0, 6-H), 6.45 (1 H, ddd, *J* 5.9, 3.2 and 1.1, 5-H), 4.86 (1 H, dd, *J* 3.4 and 0.5, 3n-H), 4.01 (1 H, t, *J* 3.6, 2x-H), 3.90 (1 H, m, 4-H), 3.86 (1 H, m, 1-H) and 3.69 (3 H, s, CO_2Me); δ_C 170.7 (C=O), 146.7 (C-7), 140.2 and 139.6 (arom C-1), 139.5 (C-6), 134.7 (C-5), 129.1, 129.1, 128.2 and 128.1 (arom C-2, -3), 127.2 (arom C-4), 126.6 (=*C*Ph_2), 87.5 (C-3), 52.4 (CO_2*Me*), 51.7 (C-4), 49.1 (C-2) and 46.1 (C-1); *m/z* 361 (M^+, 23%), 331 (52), 315 ($M^+ - NO_2$, 44), 283 (58), 255 (76), 239 (40), 230 (80), 229 (100), 228 (60), 215 (64), 165 (64) and 113 (41) (Found: M^+, 361.1311. $C_{22}H_{19}NO_4$ requires M, 361.1314).

Methyl 3-endo-*Nitro*-7-*oxo*-1,4,5,6-*tetraphenylbicyclo*[2.2.1]-*hept*-5-*ene*-2-exo-*carboxylate* **3g**.—A solution of tetraphenylcyclopentadienone (**1**; X = C=O, Y = Ph) (1.900 g, 4.94 mmol) and excess of methyl (*E*)-3-nitropropenoate (**2**; R^1 = CO_2Me, R^2 = H) (2.99 g, 22.8 mmol) in dichloromethane (20 cm^3) was kept at room temperature until the intense purple colour of the diene had faded to pale orange (24 days). Removal of the solvent under reduced pressure gave a yellow solid (4.59 g). This was triturated with warm acetone and compacted by centrifugation. Filtration gave essentially pure *methyl* 3-endo-*nitro*-7-*oxo*-1,4,5,6-*tetraphenylbicyclo*[2.2.1]*hept*-5-*ene*-2-exo-*carboxylate* **3g** (2.125 g, 83.4%), m.p. (decomp.) 181–184 °C; R_f [hexane–ethyl acetate (4:1)] 0.56. Chromatography of the filtrate on silica gel with hexane–ethyl acetate (10:1) as eluent gave a further portion of compound **3g** (30 mg, 1.2%), as well as a mixture (61:39 by NMR) of **3g** and methyl 3-*exo*-nitro-7-oxo-1,4,5,6-tetraphenylbicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylate **4g** (318 mg, 12.5%); R_f for the latter [hexane–ethyl acetate (4:1)] 0.50. A sample of the major isomer **3g** was purified for analysis by recrystallisation from dichloromethane–hexane to give rosettes, m.p. (with sintering) 182–183.5 °C (Found: C, 76.2; H, 4.85; N, 2.5. $C_{33}H_{25}NO_5$ requires C, 76.88; H, 4.89; N, 2.72%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1800 (ketone C=O), 1742 (ester C=O), 1557 and 1357 (NO_2); $\delta_H(CDCl_3)$ 7.54–7.49, 7.41–7.21, 7.15–7.01, 6.95–6.82, 6.75–6.73 and 6.60–6.54 (2, 8, 3, 3, 2 and 2 H, ArH), 6.41 (1 H, d, *J* 3.9, 3n-H), 4.21 (1 H, d, *J* 3.8, 2x-H) and 3.39 (3 H, s, CO_2Me); $\delta_C(CDCl_3)$ 192.3 (ketone C=O), 170.2 (ester C=O), 143.6 and 138.5 (alkene C), 133.2, 131.9, 131.7 and 130.2 (arom C-1), 129.9, 129.7, 129.4, 129.1, 128.2, 128.0, 127.9 and 127.6 (other arom C), 85.3 (C-3), 70.6 (C-4), 64.1 (C-1) and 52.9 and 52.6 (CO_2*Me*, C-2).

Discernible NMR signals for methyl 3-*exo*-nitro-7-oxo-1,4,5,6-tetraphenylbicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylate **4g**: $\delta_H(CDCl_3)$ (*inter alia*) 5.81 (d, *J* 3.6, 3x-H), 4.60 (d, *J* 3.6, 2n-H), 3.87 (s, CO_2Me); $\delta_C(CDCl_3)$ 193.9 (ketone C=O), 170.5 (ester C=O), 142.1 and 140.4 (alkene C), 133.3, 131.8, 131.0 and 130.6 (arom C-1), 129.8, 129.6, 128.6, 128.3, 128.2, 127.7 (two peaks) and 127.5 (other arom C), 88.0 (C-3), 66.4 and 65.2 (C-1 and -4), 53.4 (CO_2Me) and 49.5 (C-2).

3-*Nitrobicyclo*[2.2.2]*oct*-5-*ene*-2-*carbonitrile* **3h**/**4h**.—A mixture of cyclohexa-1,3-diene (**1**; X = CH_2CH_2, Y = H) (490 mg, 6.12 mmol), pyrogallol (9 mg) and (*E*)-3-nitropropenenitrile (**2**; R^1 = CN, R^2 = H) [37] (540 mg, 5.51 mmol) in dry diethyl ether (15 cm^3) was heated under reflux until the nitroalkene was consumed (21 h). Removal of the solvent under reduced pressure, followed by chromatography of the crude product (989 mg) with hexane–ethyl acetate mixtures, gave an inseparable mixture of 3-*endo*-nitrobicyclo[2.2.2]oct-5-ene-2-*exo*-carbonitrile **3h** and its 3-*exo*-nitro-2-*endo*-carbonitrile isomer **4h** (810 mg, 82%) in the 4:1 ratio (by NMR) as a waxy solid, m.p. *ca.* 150 °C; ν_{max}(KBr)/cm^{-1} 2225 (CN), 1545 and 1372 (NO_2). Major isomer: $\delta_H(CDCl_3)$ 6.43 (1 H, ddd, *J* 8.2, 6.8 and 1.5, 6-H), 6.17 (1 H, br t, *J ca.* 7.8, 5-H), 4.75 (1 H, dd, *J* 4.4 and 2.9, 3x-H), 3.49 (1 H, m, 4-H), 3.41 (1 H, m, 2n-H), 3.07 (1 H, m, 1-H), 2.1–1.9 (1 H, m, 7-H; on decoupling at δ 3.07, simplifies to ddd, *J* 12.8, 9.3 and 3.7), 1.9–1.7 and 1.65–1.43 (2 H, m, 8-H_2), 1.43–1.25 (1 H, m, 7-H); $\delta_C(CDCl_3)$ 133.8 (C-6), 129.9 (C-5), 119.1 (CN), 85.8 (C-3), 34.0 (C-4), 32.8 (C-2), 32.4 (C-1), 21.7 (C-8) and 19.2 (C-7). Discernible peaks for minor isomer: $\delta_H(CDCl_3)$ 6.53 (dd, *J* 8.6 and 2.1), 6.46 (dd?), 4.60 (ddd, *J* 4.4, 3.4 and 1.5, 3n-H), 3.72 (dd, *J* 4.4 and 2.4, 2x-H), *ca.* 3.4 (m, 4-H) and *ca.* 3.1 (m, 1-H); $\delta_C(CDCl_3)$ 134.0 and 131.9 (C-5, -6), 119.9 (CN), 86.6 (C-3), 34.4 (C-4), 32.7 (C-1), 32.3 (C-2) and 23.0 and 17.7 (C-7, -8).

3-exo,6-exo-*Dibromo*-5-endo-*hydroxy*-3-endo-*nitrobicyclo*-[2.2.1]*heptane*-2-exo-*carbonitrile* **5b**.—NBS (556 mg, 3.12 mmol) and ammonium hexafluorophosphate (1.6 mg) were added to 3-nitrobicyclo[2.2.1]hept-5-ene-2-carbonitrile [11] **3b**/**4b** (90:10 ratio) (228 mg, 1.39 mmol) in dry methanol (9 cm^3). The mixture was stirred at room temperature for 8 h, after which the solvent was removed under reduced pressure. The residue was washed with water (2 × 7.5 cm^3) and the water-insoluble material (410 mg) was recrystallised from methanol to give 3-exo,6-exo-*dibromo*-5-endo-*hydroxy*-3-endo-*nitrobicyclo*-[2.2.1]*heptane*-2-exo-*carbonitrile* **5b** (263 mg, 56%) as prisms, m.p. 186 °C (with decomposition) (Found: C, 28.1; H, 2.45; N, 8.3. $C_8H_8Br_2N_2O_3$ requires C, 28.26; H, 2.37; N, 8.24%); R_f [hexane–ethyl acetate (3:1)] 0.39; ν_{max}(KBr)/cm^{-1} 3430 (OH), 2230 (CN), 1560 and 1340 (NO_2) and 745 cm^{-1}; δ_H([$^2H_6$]-acetone) 5.39 (1 H, d, *J* 4.7, OH; exchanges with D_2O), 4.76 (1 H, m, 5x-H; on addition of D_2O, simplifies to ddd, *J* 4.6, 2.1 and 1.4), 4.53 (1 H, d, *J ca.* 0.4, 2n-H), 4.04 (1 H, m, 6n-H), 3.46 (1 H, dddd, *J* 4.6, 3.4, 1.6 and 0.4, 4-H), 3.00 (1 H, br t, *J ca.* 1.5, 1-H) and 2.53 (2 H, m, 7-H); δ_H([$^2H_6$]acetone) 117.6 (CN), 94.6 (C-3), 82.6 (C-5), 58.1 (C-4), 56.3 (C-6), 53.3 (C-1), 45.0 (C-2) and 36.6 (C-7).

Methyl 3-exo,6-exo-*Dibromo*-5-endo-*hydroxy*-3-endo-*nitro*-7-*oxabicyclo*[2.2.1]*heptane*-2-exo-*carboxylate* **5c**.—Methyl (*E*)-3-nitropropenoate (**2**; R^1 = CO_2Me, R^2 = H) (2.20 g, 16.78 mmol) and furan (2.4 cm^3, ~33 mmol) were heated at 50 °C for 2.5 h, after which excess of furan was removed under reduced pressure. The crude mixture of Diels–Alder adducts **3c**/**4c** (*ca.* 2:1; *cf.* ref. 12) was stirred with ammonium hexafluorophosphate (5 mg) and NBS (4.38 g, 24.6 mmol) in dry methanol (8 cm^3) at room temperature for 2.5 h. A precipitate began to appear after *ca.* 20 min. A further portion of NBS (600 mg, 3.37 mmol) was added, and the mixture was stirred for another 45 min. Precipitated solids (3.20 g) were removed by filtration. The methanolic filtrate was evaporated under reduced pressure; the residue obtained was washed thoroughly with water to

remove succinimide, and dried at 0.1 mmHg to give essentially pure participation product *methyl* 3-exo,6-exo-*dibromo*-5-endo-*hydroxy*-3-endo-*nitro*-7-*oxabicyclo*[2.2.1]*heptane*-2-exo-*carboxylate* **5c** (2.04 g, 32%), m.p. 198–200 °C (from acetone) (Found: C, 25.6; H, 2.4; N, 3.7. $C_8H_9Br_2NO_6$ requires C, 25.62; H, 2.42; N, 3.74%); R_f [hexane–ethyl acetate (2:1)] 0.25; ν_{max}(KBr)/cm^{-1} 3460 br (OH), 1733 (C=O), 1562 and 1356 (NO_2); δ_H([$^2H_6$]acetone) 5.76 (1 H, d, *J* 5.0, OH), 5.06 and 5.04 (2 H, m, 1- and 4-H), 4.87 (1 H, m, 5-H), 4.38 (1 H, br s, 2-H), 4.14 (1 H, d, *J* 1.5, 6-H; on decoupling at δ 5.76, simplifies to s), 3.79 (3 H, s, CO_2Me); δ_C([$^2H_6$]acetone) 168.0 (C=O), 93.6 (C-3), 88.9 and 87.6 (C-1, -4), 83.41/83.30 (C-5, Br isotope effect), 56.4 (C-2), 54.83/54.77 (^{79}Br–C-6 and ^{81}Br–C-6) and 52.9 (OMe). The precipitated solids were washed thoroughly with water, after which they were separated by chromatography with hexane–ethyl acetate mixtures to give a further quantity of compound **5c** (2.01 g, 32%) and 2-exo-*bromo*-5,5-*dimethoxy*-9-exo-*nitro*-4,8-*dioxatricyclo*[4.2.1.0^{3,7}]-*nonane* **7** (845 mg, 16%), m.p. 145–146.5 °C (from acetone) (Found: C, 34.8; H, 3.85; N, 4.5. $C_9H_{12}BrNO_6$ requires C, 34.86; H, 3.90; N, 4.52%); R_f [hexane–ethyl acetate (2:1)] 0.50; ν_{max}(KBr)/cm^{-1} 1550 and 1358 (NO_2) and 1062; δ_H([$^2H_6$]-acetone; 80 MHz) 5.41 (1 H, td, *J ca.* 4.3 and 1.4, 7-H), 5.26 (1 H, q, *J* 1.4, 1-H), 5.13 (1 H, d, *J* 1.9, 9n-H), 4.60 (1 H, br dd, *J ca.* 4.3 and 1.2, 3x-H), 4.08 (1 H, s, 2n-H), 3.45 and 3.38 (4 H, overlapping br d and s, *J ca.* 4.8, 6x-H and OMe) and 3.26 (3 H, s, OMe).

On occasion, in addition to the cyclic orthoester **7**, a quantity of the corresponding lactone 2-exo-*bromo*-9-exo-*nitro*-4,8-*dioxatricyclo*[4.2.1.0^{3,7}]*nonan*-5-*one* **6c** could be isolated: m.p. 219.5–221 °C (from acetonitrile) (Found: C, 31.75; H, 2.2; N, 5.3. $C_7H_6BrNO_5$ requires C, 31.84; H, 2.29; N, 5.30%); R_f [hexane–ethyl acetate (2:1)] 0.24; ν_{max}(KBr)/cm^{-1} 1795 (C=O) and 1548 and 1359 (NO_2); δ_H([$^2H_6$]acetone) 5.79 (1 H, td, *J* 5.0 and 1.2, 7-H; on decoupling at δ 3.75, simplifies to dd, *J* 5.0 and 1.3), 5.51 (1 H, d, *J* 1.3, 9-H), 5.48 (1 H, dd, *J* 2.2 and 1.1, 1-H), 5.13 (1 H, dt, *J* 4.9 and 0.9, 3-H; on decoupling at δ 3.75, simplifies to dd, *J* 5.0 and 1.0), 4.44 (1 H, s, 2-H), 3.75 (1 H, ddd, *J* 5.2, 2.1 and 1.1, 6-H; on decoupling at δ 5.51, simplifies to dd, *J* 4.9 and 0.8; on decoupling at δ 5.13, simplifies to dt, *J* 5.0 and 1.1); δ_C([$^2H_6$]acetone) 171.7 (C=O), 87.8 (C-1), 86.7 (C-9), 86.0 (C-3), 82.1 (C-7), 47.9 (C-2) and 45.4 (C-6).

3-exo,6-exo-*Dibromo*-6-endo-*nitro*-5-exo-*phenylbicyclo*-[2.2.1]*heptan*-2-endo-*ol* **5d**.—NBS (2.04 g, 11.45 mmol) and 5-nitro-6-phenylbicyclo[2.2.1]hept-2-ene[13] **3d**/**4d** (78:22 ratio) (1.207 g, 5.61 mmol) were stirred at room temperature in dry methanol (25 cm^3) for 5 h, after which the solvent was removed under reduced pressure. Water (45 cm^3) was added to the residue (*ca.* 3.25 g), and the mixture was extracted with dichloromethane (3 × 15 cm^3). The extracts were dried ($MgSO_4$) and evaporated, and the oil thus obtained (2.30 g) was purified by chromatography with hexane–ethyl acetate mixtures as eluent. 3-exo,6-exo-*Dibromo*-6-endo-*nitro*-5-exo-*phenylbicyclo*[2.2.1]*heptan*-2-endo-*ol* **5d** (1.416 g, 65%) was obtained as prisms, m.p. 165–166.5 °C (from benzene) (Found: C, 40.5; H, 3.6; N, 3.6. $C_{13}H_{13}Br_2NO_3$ requires C, 39.93; H, 3.35; N, 3.58%); R_f [hexane–ethyl acetate (3:1)] 0.58; ν_{max}(KBr)/cm^{-1} 3520 (OH), 1542 and 1350 (NO_2); δ_H([$^2H_6$]-acetone) 7.45–7.25 (5 H, m, ArH), 5.30 (1 H, d, *J* 4.6, OH), 4.85 (1 H, m, 2x-H; on decoupling at δ 4.11, simplifies to br t, *J ca.* 4), 4.23 (1 H, d, *J* 2.2, 5n-H), 4.11 (1 H, dd, *J* 2.7 and 2.2, 3n-H), 3.44 (1 H, dddd, *J* 4.8, 3.5, 1.4 and 0.45, 1-H), 2.91 (1 H, m, 4-H; on decoupling at δ 4.11, simplifies to quintet, *J* 1.6), 2.67 (1 H, ddt, *J* 11.9, 3.2 and 1.6, 7s-H), 2.50 (1 H, ddt?, *J* 11.9, 2.2 and 1.5, 7a-H); δ_C([$^2H_6$]acetone) 141.5 (arom C-1), 129.5 and 129.0 (arom C-2, -3), 128.4 (arom C-4), 104.4 (C-6), 83.12/83.00 (C-2, Br isotope effect), 59.66/59.60 (^{79}Br–C-3 and ^{81}Br–C-3), 57.9 (C-1), 54.4 (C-5), 53.3 (C-4) and 36.3 (C-7).

Methyl 3-exo,6-exo-*Dibromo*-5-endo-*hydroxy*-3-endo-*nitrobicyclo*[2.2.1]*heptane*-2-exo-*carboxylate* **5e**.—NBS (862 mg, 4.84 mmol) and ammonium hexafluorophosphate (3 mg) were added to a solution of methyl 3-nitrobicyclo[2.2.1]hept-5-ene-2-carboxylate **3e**/**4e** (86:14 ratio) (475 mg, 2.41 mmol) in dry methanol (5 cm^3). The mixture was stirred at room temperature for 6 h, after which the solvent was removed under reduced pressure. The residue (1.375 g) was washed with water (2 × 4 cm^3) and the water-insoluble material (796 mg) was recrystallised from benzene to give *methyl* 3-exo,6-exo-*dibromo*-5-endo-*hydroxy*-3-endo-*nitrobicyclo*[2.2.1]*heptane*-2-exo-*carboxylate* **5e** (631 mg, 70%) as prisms, m.p. 169–171 °C (Found: C, 29.0; H, 2.9; N, 3.8. $C_9H_{11}Br_2NO_5$ requires C, 28.98; H, 2.97; N, 3.76%); R_f [hexane–ethyl acetate (3:1)] 0.44; ν_{max}(KBr)/cm^{-1} 3550–3440br (OH), 1725 (C=O), 1570 and 1355 (NO_2) and 1275; δ_H($CDCl_3$) 4.74 (1 H, m, 5x-H), 4.04 (1 H, d, *J* 2.4, 2n-H), 3.81 (3 H, s, CO_2Me), 3.70 (1 H, dd, *J* 5.2 and 2.6, 6n-H), 3.35 (1 H, m, 4-H), 2.99 (1 H, m, 1-H), 2.53 (1 H, ddt, *J* 12.1, 3.1 and 1.6, 7s-H), 2.43 (1 H, ddt, *J* 12.1, 2.5 and 1.5, 7a-H) and 2.15 (1 H, d, *J* 4.1, OH); δ_H([$^2H_6$]acetone) 5.20 (1 H, d, *J* 4.7, OH; exchanges with D_2O), 4.75 (1 H, m, 5x-H; on addition of D_2O, simplifies to ddd, *J* 4.5, 2.3 and 1.4), 4.22 (1 H, br d, *J ca.* 1.4, 2n-H), 3.91 (1 H, m, 6n-H; on irradiation at δ 4.72, simplifies to dt, *J* 1.8 and 0.5), 3.76 (3 H, s, CO_2Me), 3.34 (1 H, ddd, *J* 4.6, 3.1 and 1.5, 4-H), 2.91 (1 H, m, discernible *J ca.* 1.5, 1-H) and 2.41 (2 H, m, discernible *J ca.* 1.6, 7-H_2); δ_C([$^2H_6$]acetone) 169.8 (C=O), 96.7 (C-3), 83.56/83.45 (C-5, Br isotope effect), 58.9 (C-4), 57.80/57.74 (^{79}Br–C-6 and ^{81}Br–C-6), 56.4 (C-2), 52.9 (CO_2*Me*), 51.3 (C-1) and 36.4 (C-7).

Methyl 3-exo,6-exo-*Dibromo*-7-*diphenylmethylene*-5-endo-*hydroxy*-3-endo-*nitrobicyclo*[2.2.1]*heptane*-2-exo-*carboxylate* **5f**.—NBS (272 mg, 1.53 mmol) and ammonium hexafluorophosphate (14 mg) were added to a solution of methyl 7-diphenylmethylene-3-*endo*-nitrobicyclo[2.2.1]hept-5-ene-2-*exo*-carboxylate **3f** (276 mg, 0.76 mmol) in dry methanol (5 cm^3). The mixture was stirred at room temperature for 6 h, after which the solvent was removed under reduced pressure. The residue was washed with water (4 cm^3); the water-insoluble material was dried at 0.1 mmHg to a yellow oil (369 mg) containing some unchanged NBS. Chromatography of the oil on silica gel with hexane–ethyl acetate (4:1) gave *methyl* 3-exo,6-exo-*dibromo*-7-*diphenylmethylene*-5-endo-*hydroxy*-3-endo-*nitrobicyclo*[2.2.1]*heptane*-2-exo-*carboxylate* **5f** (162 mg, 40%) as pale yellow prisms, m.p. 218–220 °C (decomp.) (from ethyl acetate–hexane) (Found: C, 49.1; H, 3.5; N, 2.6. $C_{22}H_{19}Br_2NO_5$ requires C, 49.19; H, 3.56; N, 2.61%); R_f [hexane–ethyl acetate (2:1)] 0.67; ν_{max}($CHCl_3$)/cm^{-1} 3609 (OH), 1742 (C=O), 1568 and 1350 (NO_2), 1224 and 1205; δ_H([$^2H_6$]acetone) 7.62–7.57 (2 H, m, ArH), 7.46–7.23 (8 H, m, ArH), 5.51 (1 H, d, *J* 4.7, OH), 4.96 (1 H, dm, *J ca.* 4.8, 5-H; decoupling at δ 3.64 gives dd, *J* 4.3 and 1.5), 4.34 (1 H, s, 2n-H), 4.16 (1 H, dd, *J ca.* 1.5 and 0.7, 6n-H), 3.82 (3 H, s, CO_2Me), 3.74 (1 H, ddd, *J* 4.8, 2.1 and 0.5, 4-H; decoupling at δ 3.64 gives dd, *J* 4.3 and 0.6) and 3.64 (1 H, ddd, *J* 2.0, 1.4 and 0.6, 1-H); δ_C([$^2H_6$]acetone) 169.3 (C=O), 142.1 (C-7), 140.8 and 140.3 (arom C-1), 137.1 (=*C*Ph_2), 130.5, 129.7, 129.3 and 128.7 (arom C-2, -3), 128.5 and 128.3 (arom C-4), 94.1 (C-3), 81.17/81.06 (C-5, Br isotope effect), 59.9 (C-4), 58.34/58.28 (^{79}Br–C-6 and ^{81}Br–C-6), 55.6 (C-2), 52.7 (CO_2*Me*) and 51.9 (C-1).

Methyl 6-exo-*Bromo*-5-endo-*hydroxy*-3-*nitrobicyclo*[2.2.1]-*hept*-2-*ene*-2-*carboxylate* **8e**.—A solution of methyl 3-*exo*,6-*exo*-dibromo-5-*endo*-hydroxy-3-*endo*-nitrobicyclo[2.2.1]heptane-2-*exo*-carboxylate **5e** (86 mg, 0.23 mmol) and DBU (39 mg, 0.25 mmol) in dry THF (10 cm^3) was kept at room temperature for

1 h, after which the solvent was removed under reduced pressure. The residue was partitioned between water (3 cm^3) and diethyl ether (3 × 3 cm^3). The combined organic extracts were dried ($MgSO_4$) and then evaporated under reduced pressure to give an orange oil (69 mg) that solidified on trituration with diethyl ether. Recrystallisation from benzene gave *methyl* 6-exo-*bromo*-5-endo-*hydroxy*-3-*nitrobicyclo*[2.2.1]*hept*-2-*ene*-2-*carboxylate* **8e** (42 mg, 62.5%) as bright yellow plates, m.p. 136–137 °C (Found C, 37.0; H, 3.4; N, 4.8. $C_9H_{10}BrNO_5$ requires C, 37.01; H, 3.45; N, 4.80%); R_f [hexane–ethyl acetate (3:1)] 0.40; ν_{max}(KBr)/cm^{-1} 3460 (OH), 1725 (C=O), 1525 and 1355 (NO_2) and 1280–1250br; δ_H($CDCl_3$; 80 MHz) 4.92 (1 H, m, 5-H; on addition of D_2O, simplifies to dd, *J* 4.2 and 2.2), 3.89 (3 H, s, CO_2Me), 3.75 (1 H, m, 6-H?), 3.62 (1 H, m, 4-H), 3.46 (1 H, m, 1-H?), 2.45 (1 H, d, *J* 4, OH) and 2.22 (2 H, m, 7-H_2); δ_H([$^2H_6$]acetone; 60 MHz) 5.33 (1 H, d, *J ca.* 4, OH; exchanges with D_2O), 5.00 (1 H, m, 5x-H), 3.93 (3 H, s, CO_2Me), 3.86 (1 H, m, 4-H), 3.71 (1 H, dd, *J ca.* 4 and 2, 6n-H), 3.58 (1 H, m, 1-H) and 2.31 (2 H, m, 7-H_2).

6-exo-*Bromo*-5-endo-*hydroxy*-3-*nitrobicyclo*[2.2.2]*oct*-2-*ene*-2-*carbonitrile* **8h**.—NBS (444 mg, 2.49 mg) and ammonium hexafluorophosphate (2 mg) were added to a solution of 3-nitrobicyclo[2.2.2]oct-5-ene-2-carbonitrile **3h**/**4h** (4:1 ratio) (177 mg, 0.84 mmol) in dry methanol (5 cm^3) at room temperature. After 14 h the solvent was removed under reduced pressure and the crude product was purified by chromatography with hexane–ethyl acetate as eluent. The sole characterisable product was 6-exo-*bromo*-5-endo-*hydroxy*-3-*nitrobicyclo*[2.2.2]*oct*-2-*ene*-2-*carbonitrile* **8h** (58 mg, 25%), obtained as bright yellow cubes, m.p. 179–181 °C (from ethyl acetate) (Found: C, 39.5; H, 3.2; N, 10.1. $C_9H_9BrN_2O_3$ requires C, 39.58; H, 3.32; H, 10.26%); R_f[hexane–ethyl acetate (3:1)] 0.39; ν_{max}(KBr)/cm^{-1} 3558 (OH), 2240 (CN) and 1520 and 1323 (NO_2); δ_H([$^2H_6$]acetone) 5.24 (1 H, d, *J* 4.7, OH), 4.28 (1 H, br q, *J* 3.2, 5x-H), 4.03 (1 H, q?, *J* 2.3, 6n-H), 3.73 (1 H, q?, *J* 2.9, 4-H), 3.43 (1 H, q, *J* 2.8, 1-H), 2.28 (1 H, m, 7-H; on decoupling at δ 3.43, simplifies to ddd, *J* 12.7, 9.2 and 3.3), 1.90 (1 H, m, 8-H; on decoupling at δ 3.73, simplifies to ddd, *J* 12.8, 9.3 and 5.0), 1.77 (1 H, m, 8-H; on decoupling at δ 3.73, simplifies to td, *J* 12.8 and 3.5) and 1.59 (1 H, m, 7-H); δ_C([$^2H_6$]acetone) 159.9 (C-3), 116.9 (CN), 113.9 (C-2), 79.43/79.33 (C-5, Br isotope effect), 55.07/55.00 (^{79}Br–C-6 and ^{81}Br–C-6), 45.3 (C-1), 41.3 (C-4), 21.6 (C-8) and 19.3 (C-7).

Bromination of Methyl 3-*Nitrobicyclo*[2.2.1]*hept*-5-*ene*-2-*carboxylate with Bromine in Methanol*.—A solution of bromine (184 mg, 1.15 mmol) in dry methanol (1.2 cm^3) was added dropwise during 30 min to a stirred solution of methyl 3-nitrobicyclo[2.2.1]hept-5-ene-2-carboxylate **3e**/**4e** (86:14 ratio) (218 mg, 1.11 mmol) in dry methanol (5 cm^3) containing suspended sodium hydrogen carbonate (180 mg, 2.14 mmol). The mixture was stirred for a further 4 h, after which the solvent was removed under reduced pressure. Water (10 cm^3) was added to the residue, and the mixture was extracted with dichloromethane (3 × 12 cm^3). The combined extracts were dried (Na_2SO_4) and then evaporated under reduced pressure to give an oil (358 mg). Trituration with benzene (4 cm^3) resulted in the separation of methyl 5-*exo*-bromo-6-*endo*-hydroxy-3-*exo*-methoxycarbonylbicyclo[2.2.1]heptane-2-*aci*-nitronate (**10**; R^1 = CO_2Me, X = CH_2) as a solid (138 mg, 40%), m.p. 83–86 °C, that decomposed on storage; ν_{max}(KBr)/cm^{-1} 3260br (OH), 1740 (C=O), 1672 (C=N); δ_H($CDCl_3$) 4.66 (1 H, m, 6-H), 3.83 and 3.76 (6 H, 2 × s, 2 × OMe), 3.67 (1 H, t, *J* 2.3, 5n-H), 3.57 (1 H, m, 1-H), 3.41 (1 H, m, 4-H), 2.86 (1 H, br s, 3n-H), 2.51 (1 H, br d, *J ca.* 4, OH) and 2.22–2.08 (2 H, AB pattern with fine coupling, 7-H_2).

The residue was purified by chromatography with hexane–ethyl acetate mixtures as eluent to give 5-exo-*bromo*-3-exo-*nitrobicyclo*[2.2.1]*heptane*-2,6-*carbolactone* **6e** (34 mg, 11.7%), m.p. 169–170 °C (from benzene) (Found: C, 36.5; H, 3.05; N, 5.2. $C_8H_8BrNO_4$ requires C, 36.67; H, 3.08; N, 5.34%); R_f [hexane–ethyl acetate (3:1)] 0.47; ν_{max}(KBr)/cm^{-1} 1777 (C=O), 1545 and 1350 (NO_2), 1470 and 1017; δ_H($CDCl_3$; 80 MHz) 4.99 (1 H, d, *J* 4.9, 3n-H), 4.60 (1 H, s, 6x-H), 3.80 (1 H, d, *J* 2.3, 5n-H), 3.57 (1 H, m, 1-H), 3.39 (2 H, m, 2- and 4-H), 2.45 (1 H, br d, *J ca.* 12.6, 7a-H) and 2.01 (1 H, br d, *J* 12.6 and *ca.* 1.7, 7s-H); *m*/*z* 215/217 (2%, $M^+ - NO_2$), 171/173 (31, $M^+ - NO_2 - CO_2$), 107 (25), 92 (35) and 91 (100).

Bromination of the Nitronate Ester **10**.—NBS (20 mg, 0.11 mmol) and ammonium hexafluorophosphate (0.5 mg) were stirred with methyl 5-*exo*-bromo-6-*endo*-hydroxy-3-*exo*-methoxycarbonylbicyclo[2.2.1]heptane-2-*aci*-nitronate (**10**; R^1 = CO_2Me, X = CH_2) (32.5 mg, 0.105 mmol) in dry methanol (3 cm^3) at room temperature for 18 h. The solvent was removed under reduced pressure and the residue obtained was partitioned between water (4 cm^3) and chloroform (3 × 4 cm^3). The combined extracts were dried ($MgSO_4$) and then evaporated under reduced pressure to give methyl 3-*exo*,6-*exo*-dibromo-5-*endo*-hydroxy-3-*endo*-nitrobicyclo[2.2.1]heptane-2-*exo*-carboxylate **5e** (23.5 mg, 60%) as cubes, m.p. and mixed m.p. 170–172 °C (from benzene); further characterisation as described above.

Ethyl 6-exo-*Bromo*-5-endo-*hydroxy*-3-exo-*methyl*-3-endo-*nitrobicyclo*[2.2.1]*heptane*-2-exo-*carboxylate* **11**.—Ethyl 3-*exo*-methyl-3-*endo*-nitrobicyclo[2.2.1]hept-5-ene-2-*exo*-carboxylate[10] **3a** (207 mg, 0.92 mmol), acetic acid (56 mm^3, 1 mmol) and NBS (207 mg, 1.16 mmol) were stirred together at room temperature. After 7 h, the solvent was removed under reduced pressure and the residue was purified by chromatography with hexane–diethyl ether mixtures as eluent. *Ethyl* 6-exo-*bromo*-5-endo-*hydroxy*-3-exo-*methyl*-3-endo-*nitrobicyclo*[2.2.1]*heptane*-2-exo-*carboxylate* **11** (183 mg, 62%) was obtained as prisms, m.p. 119.5–120.5 °C (from cyclohexane–ethyl acetate) (Found: C, 40.9; H, 5.1; N, 4.3. $C_{11}H_{16}BrNO_5$ requires C, 41.01; H, 5.01; N, 4.35%); R_f[hexane–diethyl ether (1:1)] 0.52; ν_{max}($CHCl_3$)/cm^{-1} 3580s and 3400br (OH), 1720 (C=O) and 1544 and 1340 (NO_2); δ_H($CDCl_3$; 80 MHz) 4.68 (1 H, quintet, *J ca.* 3.0, 5x-H; on addition of D_2O, simplifies to q, *J* 3.0), 4.22 (2 H, q, *J* 7.1, OCH_2Me), 3.92 (1 H, d, *J* 2.0, 2n-H), 3.75 (1 H, t, *J* 2.8, 6n-H), 2.84 (2 H, m, 1- and 4-H), 2.3–1.9 (2 H, AB system with further fine coupling, *J ca.* 12 and 1.2, 7-H_2), 1.87 (1 H, d, *J* 3.7, OH; exchanges with D_2O), 1.69 (3 H, s, Me) and 1.30 (3 H, t, *J* 7.1, OCH_2Me).

5-exo,6-exo-*Dibromo*-3-endo-*nitrobicyclo*[2.2.1]*heptane*-2-exo-*carbonitrile* **12**.—A solution of bromine (244 mg, 1.53 mmol) in dry chloroform (1.5 cm^3) was added during 40 min to a stirred solution of 3-nitrobicyclo[2.2.1]hept-5-ene-2-carbonitrile **3b**/**4b** (90:10 ratio) (212 mg, 1.29 mmol) in dry chloroform (4 cm^3) in which was suspended sodium hydrogen carbonate (224 mg, 2.67 mmol). After 3 h, water (10 cm^3) and a little sodium thiosulphate were added. The layers were separated, and the aq. phase was extracted with chloroform (2 × 6 cm^3). The combined organic phases were dried ($MgSO_4$), and then evaporated under reduced pressure to give a solid (417 mg) consisting of at least two components (TLC). Recrystallisation from chloroform gave a quantity of 5-exo,6-exo-*dibromo*-3-endo-*nitrobicyclo*[2.2.1]*heptane*-2-exo-*carbonitrile* **12** (122 mg, 29%), m.p. 147–148 °C (Found: C, 29.8; H, 2.4; N, 8.6. $C_8H_8Br_2N_2O_2$ requires C, 29.75; H, 2.18; N, 8.67%); R_f[hexane–ethyl acetate (3:1)] 0.58; ν_{max}(KBr)/cm^{-1} 2245 (CN) and 1555 and 1375 (NO_2); δ_H($CDCl_3$) 5.06 (1 H, t, *J* 4.3, 3x-H), 4.35 (1 H, dd, *J* 6.9 and 2.1, 5n- or 6n-H), 4.20 (1 H, dd,

J 6.9 and 2.2, 6n- or 5n-H), 3.48 (1 H, dd, *J* 4.2 and 2.8, 2n-H), 3.41 (1 H, ddd, *J* 4.8, 3.3 and 1.6, 4-H), 3.10 (1 H, br d, *J ca.* 1.5, 1-H), 2.65 (1 H, ddt, *J* 12.2, 2.9 and 1.5, 7a-H; simplifies to dt, *J* 12.1 and 1.8 on irradiation at δ 3.41), 2.02 (1 H, dddd, *J* 12.2, 3.6, 2.1 and 1.5, 7s-H; simplifies to ddd, *J* 12.1, 3.7 and 2.1 on irradiation at δ 3.41); δ_H([$^2H_6$]acetone) 5.58 (1 H, t, *J* 4.8, 3x-H), 4.78 (1 H, dd, *J* 6.9 and 2.1, 5n- or 6n-H), 4.49 (1 H, dd, *J* 6.9 and 2.1, 6n- or 5n-H), 3.75 (1 H, dd, *J* 4.9 and 3.7, 2n-H), 3.43 (1 H, ddd, *J* 4.9, 3.3 and 1.6, 4-H), 3.09 (1 H, br d, *J ca.* 1.6, 1-H), 2.51 (1 H, ddd, *J* 12.0, 2.6 and 1.7, 7a-H) and 2.12 (1 H, dddd, *J* 12.0, 3.6, 2.1 and 1.5, 7s-H); δ_C([$^2H_6$]acetone) 119.4 (CN), 88.3 (C-3), 54.53 (C-1), 54.50 (C-5 or -6; correlates with δ_H 4.78 signal), 54.0 (C-4), 50.3 (C-6 or -5; correlates with δ_H 4.49 signal), 35.5 (C-2) and 33.8 (C-7); *m/z* 244/242 (21%, M^+), 198/196 (13, $M^+ - NO_2$), 159 (60), 157 (35), 127 (100), 126 (83) and 91 (34).

Mercuriation of Ethyl 3-exo-*Methyl*-3-endo-*nitrobicyclo*[2.2.1]*hept*-5-*ene*-2-exo-*carboxylate* **3a**.—A solution of ethyl 3-*exo*-methyl-3-*endo*-nitrobicyclo[2.2.1]hept-5-ene-2-*exo*-carboxylate **3a** (93 mg, 0.41 mmol) and mercury(II) trifluoroacetate (185 mg, 0.43 mmol) in dry methanol (2 cm^3) was stirred at −23 °C for 45 min, allowed to warm to room temperature, and kept at that temperature for 16 h. Solvent was removed under reduced pressure, after which the residue was treated with aq. sodium chloride (400 mg in 7 cm^3). The mixture was extracted with ethyl acetate (3 × 7 cm^3) and the extracts were dried ($MgSO_4$) and then evaporated under reduced pressure. The crude solid thus obtained (202 mg) was purified by column chromatography on silica gel with hexane–ethyl acetate mixtures as eluent to give *ethyl* 5-exo-*chloromercurio*-6-exo-*methoxy*-3-exo-*methyl*-3-endo-*nitrobicyclo*[2.2.1]*heptane*-2-exo-*carboxylate* **14a** (97.3 mg, 48%) as needles, m.p. 177–179 °C (from ethyl acetate) (Found: C, 29.0; H, 3.75; N, 2.9. $C_{12}H_{18}ClHgNO_5$ requires C, 29.28; H, 3.69; N, 2.85%); R_f [hexane–ethyl acetate (1:1)] 0.73; ν_{max}(KBr)/cm^{-1} 1728 (C=O), 1535 and 1350 (NO_2) and 1084; δ_H([$^2H_6$]acetone; 80 MHz) 4.19 (2 H, q, *J* 7.1, CO_2CH_2Me), 3.61 (1 H, d, *J* 7.4, 6n-H), 3.40 (3 H, s, OMe), 3.06, 2.95 and 2.78 (3 H, 3 × m, 1-, 2n- and 4-H), 2.58 (1 H, br d, *J ca.* 7.3, 5n-H), 1.92 (2 H, m, 7-H_2), 1.68 (3 H, s, 3x-Me) and 1.26 (3 H, t, *J* 7.1, CO_2CH_2Me); and *ethyl* 6-exo-*chloromercurio*-5-endo-*hydroxy*-3-exo-*methyl*-3-endo-*nitrobicyclo*[2.2.1]*heptane*-2-exo-*carboxylate* **13a** (28 mg, 14%) as spars, m.p. 201–203 °C (from ethyl acetate) (Found: C, 27.3; H, 3.45; N,, 3.0. $C_{11}H_{16}ClHgNO_5$ requires C, 27.62; H, 3.37; N, 2.93%); R_f [hexane–ethyl acetate (1:1)] 0.60; ν_{max}(KBr)/cm^{-1} 3485 (OH), 1728 (C=O), 1535 and 1352 (NO_2); δ_H($CDCl_3$; 80 MHz) 4.19 (2 H, q, *J* 7.1, CO_2CH_2Me), 4.06 (1 H, d, *J* 6.8, 5x-H), 3.41 (1 H, br d, *J ca.* 1.4, 4-H), 2.92 (1 H, br d, *J ca.* 1.4, 2n-H), 2.59 and ~2.51 (2 H, m and dd, *J* 6.8 and 2.4, 1- and 6n-H), 2.32 (1 H, d, *J* 2.4, OH; exchanges with D_2O), 1.98 (2 H, m, 7-H_2), 1.68 (3 H, s, 3x-Me) and 1.28 (3 H, t, *J* 7.1, CO_2CH_2Me).

Mercuriation of Methyl 3-endo-*Nitrobicyclo*[2.2.1]*hept*-5-*ene*-2-exo-*carboxylate* **3e**.—A solution of methyl 3-*endo*-nitrobicyclo[2.2.1]hept-5-ene-2-*exo*-carboxylate **3e** (202 mg, 1.02 mmol) and mercury(II) trifluoroacetate (456 mg, 1.13 mmol) in dry methanol (7.5 cm^3) was stirred at −20 °C for 1 h and at 0 °C for 12 h. Solvent was removed under reduced pressure, after which the residue was treated with aq. sodium chloride (0.3 g in 10 cm^3). The mixture was extracted with diethyl ether (3 × 10 cm^3) and the extracts were dried ($MgSO_4$) and then evaporated under reduced pressure. The crude solid thus obtained (499 mg) was purified by column chromatography on silica gel with hexane–ethyl acetate mixtures as eluent to give *methyl* 5-exo-*chloromercurio*-6-exo-*methoxy*-3-endo-*nitrobicyclo*[2.2.1]*heptane*-2-exo-*carboxylate* **14e** (349 mg, 71%) as spars, m.p. 171–172 °C (from benzene) (Found: C, 25.6; H, 3.1; N, 3.0. $C_{10}H_{14}ClHgNO_5$ requires C, 25.87; H, 3.04; N, 3.02%); R_f [hexane–ethyl acetate (1:1)] 0.54; ν_{max}(KBr)/cm^{-1} 1720 (C=O), 1543 and 1381 (NO_2) and 1210; δ_H([$^2H_6$]acetone) 5.29 (1 H, dd with ^{199}Hg satellites, $^4J_{H-Hg}$ 67.8, $^3J_{H-H}$ 4.9 and 4.2, 3x-H), 3.73 (4 H, s and br d, *J ca.* 6.7, CO_2Me and 6n-H), 3.44 (4 H, s and m, OMe and 4-H), 2.99 and 2.97 (2 H, br d and dd?, *J ca.* 2 and *ca.* 4 and 2.3, 1- and 2n-H), 2.74 (1 H, dd, *J* 6.8 and 2.7, 5n-H), 1.88 (1 H, ddd, *J* 11.0, 3.9 and 1.7, 7a-H) and 1.57 (1 H, ddq, *J* 11.0, 2.8 and 1.4, 7s-H); δ_C([$^2H_6$]acetone) 173.3 (C=O), 90.8 (C-3), 86.1 (C-6), 57.2 (6-OMe), 55.3 (C-5), 53.2 (CO_2Me), 46.9 (C-1), 46.8 (C-4), 45.3 (C-2) and 35.1 (C-7); and *methyl* 6-exo-*chloromercurio*-5-endo-*hydroxy*-3-endo-*nitrobicyclo*[2.2.1]*heptane*-2-exo-*carboxylate* **13e** as an oil (92 mg, 20%) that slowly crystallised on storage. An analytically pure sample was obtained by recrystallisation from benzene–ethyl acetate, m.p. 117–119 °C (Found: C, 23.7; H, 2.75; N, 3.1. $C_9H_{12}ClHgNO_5$ requires C, 24.01; H, 2.69; N, 3.11%); R_f [hexane–ethyl acetate (1:1)] 0.40; ν_{max}(KBr)/cm^{-1} 3480br (OH), 1720 (C=O) and 1530 (NO_2); δ_H([$^2H_6$]acetone; 80 MHz) 5.26 (1 H, t, *J* 4.6, 3x-H), 5.06 (1 H, d, *J* 2.9, OH; exchanges with D_2O), 4.14 (1 H, br d, *J ca.* 6.3, 5x-H), 3.71 (3 H, s, CO_2Me), 3.46 (1 H, dd, *J* 4.4 and 1.4, 4-H), 2.98 (1 H, dd, *J* 4.9 and 2.4, 6n-H), 2.76 (2 H, m, 1- and 2n-H), ~2.1 (7-H, obscured by solvent) and 1.55 (1 H, dm, *J ca.* 11.8, 7-H).

Acknowledgements

We thank the Foundation for Research Development for generous funding for this research; the Foundation for Research Development and the University of the Witwatersrand for research bursaries to NFB; the CSIR, Pretoria, for mass spectra and microanalyses; Dr. L. Carlton and Mrs. S. Heiss of this Department for invaluable assistance in obtaining NMR spectra; and Mr. Peter Wright for assistance with some of the syntheses.

References

1 Part 7: J. P. Michael, T. L. Maqutu and A. S. Howard, *J. Chem. Soc., Perkin Trans. 1*, 1989, 2389.
2 G. Haufe, F. Gierscher, G. Köhler and K. Schulze, *J. Prakt. Chem.*, 1987, **329**, 817, and references cited therein.
3 H. B. Henbest and B. Nicholls, *J. Chem. Soc.*, 1959, 221.
4 J. J. Périé, J. P. Laval, J. Roussel and A. Lattes, *Tetrahedron Lett.*, 1971, 4399.
5 S. Knapp, K. E. Rodriquez, A. T. Levorse and R. M. Ornaf, *Tetrahedron Lett.*, 1985, **26**, 1803.
6 A. Factor and T. G. Traylor, *J. Org. Chem.*, 1968, **33**, 2607.
7 M. Cinquini, S. Colonna and F. Montanari, *J. Chem. Soc. C*, 1970, 572.
8 J. I. G. Cadogan, D. K. Cameron, I. Gosney, R. M. Highcock and S. F. Newlands, *J. Chem. Soc., Chem. Commun.*, 1986, 766.
9 N. F. Blom, D. M. F. Edwards, J. S. Field and J. P. Michael, *J. Chem. Soc., Chem. Commun.*, 1980, 1240.
10 C. Shin, Y. Kosuge, M. Yamaura and J. Yoshimura, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 1137.
11 J. P. Michael and N. F. Blom, *J. Chem. Soc., Perkin Trans. 1*, 1989, 623.
12 G. Just and M. Lim, *Can. J. Chem.*, 1977, **55**, 2993.
13 W. E. Parham, W. T. Hunter and R. Hanson, *J. Am. Chem. Soc.*, 1951, **73**, 5068.
14 S. S. Novikov, G. A. Shvekhgeimer and A. A. Dudinskaya, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1961, 690; English translation in *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1961, 640.
15 A. P. Marchand, *Stereochemical Applications of NMR Studies in Rigid Bicyclic Systems*, Verlag Chemistry International, Deerfield Beach, 1982.
16 J. P. Michael, N. F. Blom and J. C. A. Boeyens, *J. Chem. Soc., Perkin Trans. 1*, 1984, 1739.
17 D. Ranganathan, C. B. Rao, S. Ranganathan, R. K. Mehrotra and R. Iyengar, *J. Org. Chem.*, 1980, **45**, 1185.
18 A. T. Nielsen, in *The Chemistry of the Nitro and Nitroso Groups*, Part 1, ed. H. Feuer, Interscience, New York, 1969, pp. 417–430.

19 G. V. Roitburd, W. A. Smit, A. V. Semenovsky, A. A. Shchegolev, V. F. Kucherov, O. S. Chizhov and V. I. Kadentsev, *Tetrahedron Lett.*, 1972, 4935.
20 M. B. Gravestock, D. R. Morton, S. G. Boots and W. S. Johnson, *J. Am. Chem. Soc.*, 1980, **102**, 800.
21 P. N. Preston and G. Tennant, *Chem. Rev.*, 1972, **72**, 627.
22 Y. S. Shabarov, S. S. Mochalov, T. S. Oretskaya and V. V. Karpova, *J. Organomet. Chem.*, 1978, **150**, 7, and references cited therein.
23 J. M. Bakke, *Acta Chem. Scand., Ser. B*, 1975, **29**, 1063.
24 T. W. M. Spence and G. Tennant, *J. Chem. Soc. C*, 1971, 3712.
25 S. S. Ball, L. J. Andrews and R. M. Keefer, *J. Org. Chem.*, 1979, **44**, 525, and references cited therein.
26 P. Brownbridge, P. K. G. Hodgson, R. Shepherd and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, 1976, 2024.
27 T.-L. Ho, *J. Chem. Soc., Chem. Commun.*, 1980, 1149.
28 Y. S. Shabarov, S. S. Mochalov and V. I. Daineko, *J. Org. Chem. USSR*, 1976, **12**, 1289.
29 M. Finkelstein, S. A. Hart, W. M. Moore and S. D. Ross, *J. Org. Chem.*, 1986, **51**, 3548, and references cited therein.
30 T. G. Traylor, *Acc. Chem. Res.*, 1969, **2**, 152.
31 H. Kwart and L. Kaplan, *J. Am. Chem. Soc.*, 1954, **76**, 4078; R. Caple, F. M. Hsu and C. S. Ilenda, *J. Org. Chem.*, 1968, **33**, 4111; R. Caple, G. M.-S. Chen and J. D. Nelson, *J. Org. Chem.*, 1971, **36**, 2870.
32 J. C. A. Boeyens, L. Denner and J. P. Michael, *J. Chem. Soc., Perkin Trans. 2*, 1984, 767.
33 H. Kessler, C. Griesinger, J. Zarbock and H. R. Loosli, *J. Magn. Reson.*, 1984, **57**, 331.
34 F. A. L. Anet, *Tetrahedron Lett.*, 1964, 3339; A. McKillop, M. E. Ford and E. C. Taylor, *J. Org. Chem.*, 1974, **39**, 2434.
35 R. R. Fraser, M. Kaufman, P. Morand and G. Govil, *Can. J. Chem.*, 1969, **47**, 403.
36 W. C. Still, M. Kahn and A. Mitra, *J. Org. Chem.*, 1978, **43**, 2923.
37 H. Shechter, F. Conrad, A. L. Daulton and R. B. Kaplan, *J. Am. Chem. Soc.*, 1952, **74**, 3052.

Paper 1/00208B
Received 15*th January* 1991
Accepted 27*th February* 1991