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Rearrangement and Participation Reactions occurring during the Bromination of 7-Trimethylsilylnitronorbornenes. Evidence for a Discrete Carbocation β to Silicon

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Transannular neighbouring group participation by the *endo*-substituent occurs during bromination at the double bonds of methyl 3-*endo*-nitro-7-*anti*-trimethylsilylbicyclo[2.2.1]hept-5-ene-2-*exo*-carboxylate (**12**), the corresponding *exo*-nitro-*endo*-carboxylate isomer (**15**), and the *exo*-nitro-*endo*-methanol analogue (**16**). Silicon-assisted Wagner–Meerwein rearrangement occurs as a minor reaction for (**12**), but becomes the major pathway in the bromination of 5-*endo*-nitro-7-*anti*-trimethylsilylbicyclo[2.2.1]hept-2-ene (**2**) and 3-*endo*-nitro-7-*anti*-trimethylsilylbicyclo[2.2.1]hept-5-en-2-*exo*-ylmethanol (**3**). In the latter case, both 7-*anti*-bromo-3-*exo*-nitrobicyclo[2.2.1]hept-5-en-2-*endo*-ylmethanol (**10**) and a tricyclic ether (**11**) are formed. The structure of (**11**) was confirmed by *X*-ray crystallography. Evidence is presented for the involvement of a discrete carbocation β to silicon in this rearrangement.

The β-effect[1] of organosilicon substituents—the stabilisation of an incipient or full positive charge on an atom β to silicon—is generally ascribed to hyperconjugation between the polarised Si–C(α) bond and an empty orbital or its equivalent on the β-atom, and is consequently subject to a geometrical demand which is usually easily satisfied. The phenomenon underlies the outstanding regioselectivity manifested in the reactions of many organosilicon compounds, for example, in the reaction of vinyl- and allyl-silanes with electrophiles,[2] where the generation of a C=C bond by the loss of silicon to a nucleophile often completes the reaction. Formal cationic intermediates are frequently invoked in these reactions, but the evidence for their discrete intermediacy is rare.[3] In many cases the reactions can instead be envisaged as concerted processes in which the joint operation of favourable electronic and stereoelectronic effects facilitates the attainment of an appropriate transition state.

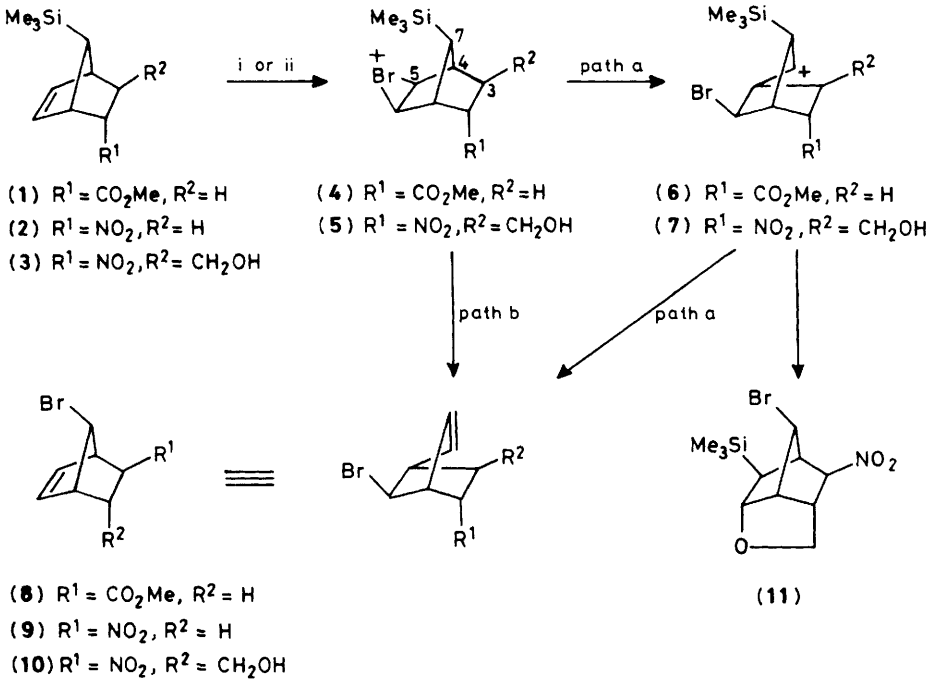
We have previously used the β-cation formalism[4] to rationalise the outcome of the silicon-controlled Wagner–Meerwein rearrangement of 7-trimethylsilylnorbornenes under the action of electrophiles, for example, in the conversion of the norbornenyl ester (**1**) into the bromonorbornene (**8**) *via* intermediates (**4**) and (**6**) (Scheme 1, path a).[5] In principle, however, this reaction might actually proceed in a concerted fashion (path b), since the migrating bond in compound (**4**), C(4)–C(3), is antiperiplanar to both the Si–C(7) bond and to the C(5)–Br bond. The generation of the double bond in the product (**8**) is effectively then an *E*2 elimination of Si and C(3), while the carbon–carbon bond migration effectively involves an S_N2 displacement of bromine from C(5). We have now investigated a variant of the silicon-assisted Wagner–Meerwein rearrangement which seems to provide evidence for a silicon-stabilised carbocation as a genuine intermediate.

Results and Discussion

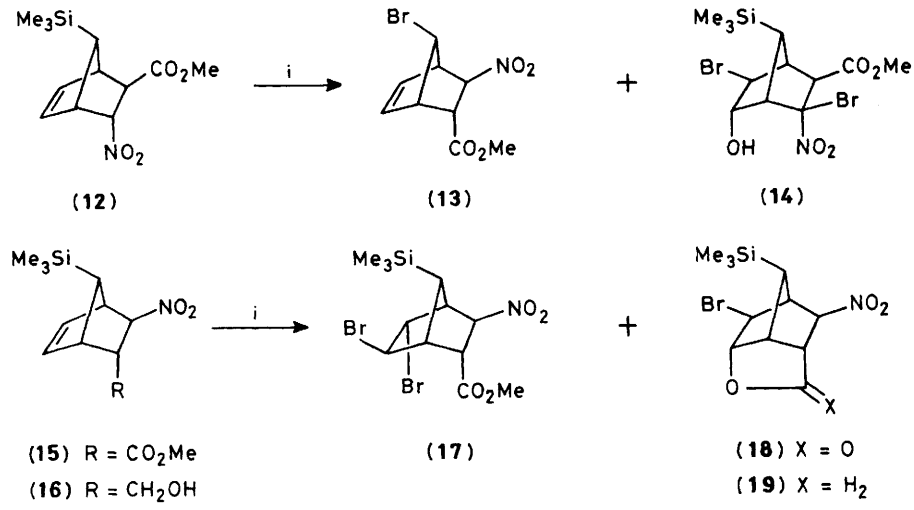
The substrates on which this investigation is based were prepared from methyl (*E*)-3-nitropropenoate[6] which, like other potent dienophiles,[7] captures the most abundant isomer of trimethylsilylcyclopentadiene.[8] When this Diels–Alder reaction was performed under mild conditions (diethyl ether, room temperature, 3 h), the ratio of the *endo*- and *exo*-nitro isomer (**12**) and (**15**) in the crude adduct mixture was found to be 80:20 by n.m.r. spectroscopy. This ratio is similar to the 84:16 ratio of *endo*- and *exo*-nitro isomers reported for the reaction of the same dienophile with cyclopentadiene.[9] In agreement with the predictions of Kakushima and Scott[10] (but in contrast to a similar reaction reported by Danishefsky and co-workers[11]), secondary orbital interactions involving the nitro group probably control the stereochemical outcome of the reaction. The isomers (**12**) and (**15**) could be separated by means of medium pressure preparative liquid chromatography.

Bromination of the *endo*-nitro adduct (**12**) with *N*-bromosuccinimide (NBS) in methanol, a source of electrophilic bromine, was a poor reaction (Scheme 2). Silicon-assisted Wagner–Meerwein rearrangement was certainly not the sole reaction pathway, and the rearranged product, (**13**), was isolated after column chromatography in only 21% yield. A second identifiable product, (**14**) (18%), results from nitro group participation, a highly unusual reaction which we have reported elsewhere.[9,12] In the case of the *exo*-nitro isomer (**15**), no rearrangement product at all could be detected on bromination under similar conditions; the reaction was very slow (18 days at room temperature), and only the dibromo product (**17**) (33%) and the lactone (**18**) (27%) were isolated. These results are in line with our previous findings[5] concerning the bromination of the Diels–Alder adduct of trimethylsilylcyclopentadiene and dimethyl fumarate. In all three cases, the presence of strongly electron-withdrawing groups on both C(2) and C(3) seems to inhibit the migration of these atoms, and thereby suppress skeletal rearrangement; participation by the *endo*-functional group is responsible for a high proportion of the isolable product.

The situation was radically changed when one of these electron-withdrawing groups was removed or modified. For example, the major Diels–Alder adduct (**2**) from the reaction of nitroethene and trimethylsilylcyclopentadiene[13] quantitatively afforded the cleanly rearranged product (**9**) on treatment with NBS in methanol. More importantly from the mechanistic viewpoint, the *endo*-nitronorbornen-*exo*-ylmethanol (**3**), prepared in 41% yield from compound (**12**) and lithium aluminium hydride, yielded two products on treatment with NBS in methanol. The major product (**10**) (47%) results from the expected rearrangement; the minor product (37%) was a tricyclic silylated ether, tentatively assigned as structure (**11**) on the basis of the n.m.r. spectra. In view of the mechanistic implications attendant on the isolation of this product, we



Scheme 1. *Reagents:* i, Br_2, MeOH [(**1**) only]; ii, NBS, MeOH [(**2**) and (**3**) only]



Scheme 2. *Reagents:* i, NBS, MeOH

confirmed its structure (see Figure) by *X*-ray crystallography. The fractional atomic co-ordinates and equivalent thermal vibration parameters for non-hydrogen atoms (Table 1) and selected bond lengths (Table 2) are given. Full tables of bond lengths, bond angles, and anisotropic temperature factors, and the fractional atomic co-ordinates for the hydrogen atoms, are available as a Supplementary Publication (SUP No. 23977, 12 pp.).*

It is improbable that the migration of C(3) to C(5) in the bromonium ion intermediate (**5**) is concerted with the attack of the OH group on to C(4) (Scheme 1, path b). Not only must both processes occur at C(4) in a stereoelectronically unlikely synperiplanar fashion, but the transition state formed thereby would be considerably strained. The only plausible course of events is by path a: bond migration of C(3) to C(5) must occur prior to ether formation, and this in turn implies carbocation intermediacy at C(4), that is, β to silicon. The antiperiplanar arrangement of the Si–C(7) and C(4)–C(3) bonds in the intermediate (**5**) means that minimal molecular reorganisation is necessary in order to achieve the correct orbital overlap for stabilising the carbocation (**7**). Once the migration has been accomplished, the OH group is poised for easy capture of the cation, giving the tricyclic compound (**11**); alternatively, loss of silicon (presumably to the solvent) yields the rearranged norbornene (**10**).

Silicon-assisted Wagner–Meerwein rearrangement need not always be the preferred reaction pathway even when structural features might appear to operate in its favour. When the *exo*-nitronorbornen-*endo*-ylmethanol (**16**) was treated with NBS in methanol, rearrangement failed to occur, not because it is intrinsically disfavoured [after all, the isomer (**3**) rearranges readily, as we showed above], but because the pendent

* For details of the Supplementary Publications Scheme see Instructions for Authors (1984) in *J. Chem. Soc., Perkin Trans. 1*, 1984, Issue 1.

Table 1. Fractional atomic co-ordinates (Å × 10^4) and equivalent thermal vibrational parameters (× 10^3/Å^2) of the non-hydrogen atoms of compound (**11**) with e.s.d.s in parentheses

	x	*y*	*z*	U_{eq}
C(1)	498(15)	4 336(9)	1 547(8)	38(5)
O(2)	−519(10)	5 439(8)	1 736(7)	54(5)
C(3)	1 060(18)	6 738(12)	2 149(12)	60(8)
C(4)	3 153(16)	6 414(11)	2 114(9)	46(6)
C(5)	3 902(15)	5 804(10)	3 233(9)	38(5)
C(6)	3 419(14)	4 214(10)	2 919(8)	37(5)
C(7)	4 093(16)	4 279(10)	1 661(8)	40(6)
C(8)	2 655(15)	5 120(10)	1 191(8)	39(5)
C(9)	997(14)	3 676(9)	2 718(8)	34(5)
N(10)	6 226(14)	6 473(10)	3 618(8)	50(6)
O(11)	7 054(14)	7 678(10)	3 344(10)	88(7)
O(12)	7 137(12)	5 806(10)	4 216(8)	70(6)
Br(13)	3 638(2)	2 420(1)	755(1)	59(1)
Si(14)	9 666(4)	1 680(3)	2 855(3)	41(2)
C(15)	−2 319(19)	1 735(15)	3 920(13)	63(6)
C(16)	−1 704(23)	664(14)	1 456(12)	64(9)
C(17)	1 524(20)	750(14)	3 510(14)	61(8)

Table 2. Bond lengths (Å) for bonds containing non-hydrogen atoms for compound (**11**), with e.s.d.s in parentheses

C(1)–O(2)	1.430(11)	C(6)–C(9)	1.558(13)
C(1)–C(8)	1.537(13)	C(7)–C(8)	1.507(14)
C(1)–C(9)	1.561(13)	C(7)–Br(13)	1.959(8)
O(2)–C(3)	1.435(13)	C(9)–Si(14)	1.920(9)
C(3)–C(4)	1.520(15)	N(10)–O(11)	1.221(12)
C(4)–C(5)	1.538(14)	N(10)–O(12)	1.204(12)
C(4)–C(8)	1.533(14)	Si(14)–C(15)	1.876(12)
C(5)–C(6)	1.502(13)	Si(14)–C(16)	1.860(13)
C(5)–N(10)	1.532(13)	Si(14)–C(17)	1.858(13)
C(6)–C(7)	1.532(13)		

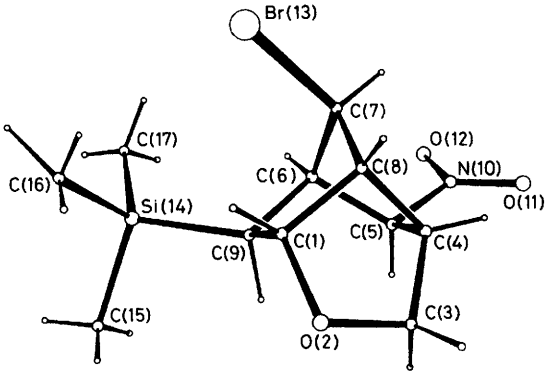


Figure. ORTEP-generated diagram for (5*R**,7*R**,9*R**)-7-bromo-5-nitro-9-trimethylsilyl-2-oxatricyclo[2.2.1.$0^{4,8}$]nonane (**11**) showing the crystallographic numbering scheme adopted for the non-hydrogen atoms

hydroxymethyl group is a sufficiently good nucleophile to participate in a transannular reaction, yielding the tricyclic ether (**19**) (95%). Compound (**19**) is an isomer of the tricycle (**11**), and a comparison of the ^{1}H n.m.r. spectra of the two in conjunction with decoupling experiments allowed unambiguous assignment of the stereochemistries of both.

Experimental

N.m.r. spectra were recorded on a Bruker WP-80 or Varian EM-360A instrument. Results are reported on the δ scale relative to Me_4Si. In most cases, extensive decoupling experiments allowed the unambiguous assignment of signals. I.r. spectra were recorded on a Pye-Unicam SP3-300 spectrometer using the potassium bromide dispersion technique for solid samples; liquids were run as films between sodium chloride plates. Mass spectra were obtained on a Varian-MAT CH-7 instrument, and accurate mass determinations were performed on a Varian MAT-212 instrument. Thin-layer chromatograms were run on Merck DC-Fertigplatten Kieselgel F-254 plates.

Diels–Alder Reaction between Methyl (E)-3-*Nitropropenoate and Trimethylsilylcyclopentadiene.*—Trimethylsilylcyclopentadiene (2.14 g, 15.5 mmol) in dry diethyl ether (5 ml) was added at room temperature to a solution of the nitroalkene (1.85 g, 14.1 mmol) in diethyl ether (30 ml). After 3 h the solvent was removed by evaporation under reduced pressure, leaving a colourless oil (3.98 g), an n.m.r. spectrum of which indicated an *endo*/*exo*-nitro isomer ratio of 80:20. Medium pressure preparative liquid chromatography of a portion of this product (3.00 g) on ICN Kieselgel Woelm (0.032—0.063 mm) packed into two LC Cheminert glass columns (a scrubber column, 12.7 × 265 mm, followed by the main column, 12.7 × 960 mm) using, as eluant, diethyl ether–hexane (1:9 v/v) under a pressure of 40 lb in^{-2} afforded chromatographically homogeneous samples of *methyl* 3-endo-*nitro*-7-anti-*trimethylsilylbicyclo*[2.2.1]*hept*-5-*ene*-2-exo-*carboxylate* (**12**) (2.13 g, 75% effective yield), and *methyl* 3-exo-*nitro*-7-anti-*trimethylsilylbicyclo*[2.2.1]*hept*-5-*ene*-2-endo-*carboxylate* (**15**) (0.58 g, 20% effective yield). The former compound, (**12**), was obtained as a yellow oil, a sample of which was purified for microanalysis by distillation at 110—130 °C/1.5 mmHg (Found: C, 53.0; H, 7.0; N, 5.1. $C_{12}H_{19}NO_4Si$ requires C, 53.5; H, 7.1; N, 5.2%), R_F (hexane–diethyl ether 4:1, v/v) 0.55; $\nu_{max.}$(film) 1 728 (C=O), 1 540 and 1 370 (NO_2), and 1 250 and 840 cm^{-1} ($SiMe_3$); δ($CDCl_3$) 6.37 (1 H, dd, *J* 5.6 and 3.0 Hz, 6-H), 5.97 (1 H, dd, *J* 5.6 and 2.8 Hz, 5-H), 5.35 (1 H, t, *J* 3.8 Hz, 3-H), 3.74 (3 H, s, CO_2Me), 3.61 (1 H, m, 4-H), 3.25 (1 H, m, 1-H), 3.06 (1 H, d, *J* 3.8 Hz, 2-H), 1.32 (1 H, s, 7-H-*syn*), and −0.08 (9 H, s, $SiMe_3$); *m*/*z* 254 (14%, M^+ − Me), 223 (14, M^+ − NO_2), 138 (13), 123 (20), 119 (92), and 73 (100). The latter compound, (**15**), was a labile oil which partly solidified on standing (m.p. 24—28 °C); R_F (hexane–diethyl ether 4:1 v/v) 0.47; $\nu_{max.}$(film) 1 734 (C=O), 1 544 and 1 365 (NO_2), and 1 250 and 840 cm^{-1} ($SiMe_3$); δ($CDCl_3$) 6.17 (2 H, t, *J* 1.9 Hz, 5-H and 6-H), 4.73 (1 H, d, *J* 3.5 Hz, 3-H), 3.72 and 3.69 (4 H, m, and s, 2-H and CO_2Me), 3.54 (1 H, m, 1-H or 4-H), 3.39 (1 H, m, 1-H or 4-H), 1.53 (1 H, br s, 7-H-*syn*), and −0.04 (9 H, s, $SiMe_3$); *m*/*z* 254 (7%, M^+ − Me), 223 (9, M^+ − NO_2), 138 (13), 123 (8), 119 (95), and 73 (100).

Bromination of the endo-*Nitro Compound* (**12**).—*N*-Bromosuccinimide (804 mg, 4.52 mmol) and ammonium hexafluorophosphate (1.5 mg) were added to a solution of the *endo*-nitro compound (**12**) (503 mg, 1.87 mmol) in dry methanol (4 ml). The solution was left at room temperature for 10 h, then heated under reflux for 3.5 h, after which the solvent was removed under reduced pressure. The residue was partitioned between water (35 ml) and diethyl ether (3 × 10 ml); the combined organic phases were dried ($MgSO_4$) and evaporated under reduced pressure to a semi-solid (243 mg) which was purified by chromatography on silica gel using hexane–diethyl ether mixtures. Three homogeneous products were obtained, as well as some fractions containing mixtures of unidentifed materials: recovered starting material (**12**) (34 mg, 7%); *methyl* 3-exo,6-exo-*dibromo*-5-endo-*hydroxy*-3-endo-*nitro*-7-anti-*trimethylsilylbicyclo*[2.2.1]*heptane*-2-exo-*carboxylate* (**14**) (155 mg, 18%), a sample of which was purified for characterisation by recrystallisation from cyclohexane–benzene followed by sublimation at 150 °C/1 mmHg, m.p. 181—182.5 °C (Found: C, 32.2; H, 4.3; N, 3.1. $C_{12}H_{19}Br_2NO_5Si$ requires C, 32.4; H, 4.3; N,

3.2%), R_F (hexane–ethyl acetate 3:1, v/v) 0.43; $\nu_{max.}$(KBr) 3 505 (OH), 1 726 (C=O), 1 564 and 1 350 (NO_2), and 1 240 and 846 cm^{-1} ($SiMe_3$); δ($CDCl_3$) 4.84 (1 H, br dd, *J ca.* 4 and 8 Hz, 5-H), 4.14 (1 H, s, 2-H), 3.80 (3 H, s, CO_2Me), 3.68 (1 H, t, *J* 3 Hz, 6-H), 3.33 and 3.04 (2 × 1 H, br m, 1-H and 4-H), 2.14 (1 H, br m, 7-H), 1.95 (1 H, d, *J* 4 Hz, OH, exchanges with D_2O), and 0.26 (9 H, s, $SiMe_3$) *m/z* 364/366 (0.6%, M^+ − Br), 317/319 (2, M^+ − Br − HNO_2), and 73 (100); and *methyl* 7-anti-*bromo*-3-exo-*nitrobicyclo*[2.2.1]*hept*-5-*ene*-2-endo-*carboxylate* (**13**) (106 mg, 21%) as an oil which slowly crystallised on seeding. An analytically pure sample was obtained as prisms, m.p. 77—78 °C (from di-isopropyl ether) (Found: C, 39.2; H, 3.7; N, 5.1. $C_9H_{10}BrNO_4$ requires C, 39.2; H, 3.65; N, 5.1%); R_F (hexane–ethyl acetate 3:1, v/v) 0.38; $\nu_{max.}$(KBr) 1 744 (C=O), 1 546 and 1 370 cm^{-1} (NO_2); δ($CDCl_3$) 6.24 (2 H, m, 5-H and 6-H), 4.77 (1 H, d, *J* 4 Hz, 3-H), 4.46 (1 H, br s, 7-H), 3.74 and 3.55 (6 H, s and m, CO_2Me, 1-H, 2-H, and 4-H); *m/z* 275/277 (2%, M^+), 229/231 (31, M^+ − NO_2), 91 (73), and 73 (100).

Bromination of the exo-*Nitro Compound* (**15**).—*N*-Bromosuccinimide (87 mg, 0.49 mmol) and ammonium hexafluorophosphate (0.1 mg) were added to a solution of the *exo*-nitro compound (**15**) (61 mg, 0.22 mmol) in dry methanol (2 ml). The mixture was left to stand at room temperature for 18 days, after which time t.l.c. showed that the starting material had been consumed. The solvent was evaporated, and the crude product (151 mg) was chromatographed on silica gel, eluting with hexane–ethyl acetate mixtures. Two products were obtained: 5-exo-*bromo*-3-exo-*nitro*-7-anti-*trimethylsilylbicyclo*-[2.2.1]*heptane*-2,6-*carbolactone* (**18**) (20 mg, 27%) as colourless needles, m.p. 144—146 °C (from benzene) (Found: C, 39.4; H, 4.9; N, 4.2. $C_{11}H_{16}BrNO_4Si$ requires C, 39.5; H, 4.8; N, 4.2%), R_F (hexane–ethyl acetate 3:1, v/v) 0.07; $\nu_{max.}$(KBr) 1 795 (C=O), 1 553 and 1 370 (NO_2), and 1 249 and 836 cm^{-1} ($SiMe_3$); δ($CDCl_3$) 5.00 (1 H, d, *J* 4.6 Hz, 3-H), 4.62 (1 H, br s, 6-H), 3.72 (1 H, d, *J* 2.2 Hz, 5-H), 3.53 and 3.50 (3 H, br s and m, 1-H, 2-H, and 4-H), 1.43 (1 H, br s, 7-H), and 0.25 (9 H, s, $SiMe_3$); *m/z* 318/320 (6%, M^+ − Me), 137/139 (41), 91 (41), and 73 (100); and *methyl* 5-endo,6-exo-*dibromo*-3-exo-*nitro*-7-anti-*trimethylsilylbicyclo*[2.2.1]*heptane*-2-endo-*carboxylate* (**17**) (31 mg, 32%), as colourless needles, m.p. 102—103 °C (from hexane) (Found: C, 33.3; H, 4.4; N, 3.2. $C_{12}H_{19}Br_2NO_4Si$ requires C, 33.6; H, 4.5; N, 3.3%); R_F (hexane–ethyl acetate 3:1, v/v) 0.56; $\nu_{max.}$(KBr) 1 740 (C=O), 1 550 and 1 379 (NO_2), and 1 247, 842, and 831 cm^{-1} ($SiMe_3$); δ($CDCl_3$) 5.50 (1 H, d, *J* 4.5 Hz, 3-H), 4.55 (1 H, t, *J* 4.5 Hz, 5-H), 3.82 (4 H, m, CO_2Me and 6-H), 3.66 (1 H, t, *J* 4.5 Hz, 2-H), 3.28 (1 H, br d, *J* 4.5 Hz, 4-H), 3.08 (1 H, br d, *J* 4.5 Hz, 1-H), 1.37 (1 H, m, 7-H), and 0.25 (9 H, s, $SiMe_3$); *m/z* 412/414/416 (6/15/7%, M^+ − Me), 197/199 (32), 149 (56), 137/139 (47), 119 (33), 91 (65), and 73 (100).

7-syn-*Bromo*-5-exo-*nitrobicyclo*[2.2.1]*hept*-2-*ene* (**9**).—A mixture of *N*-bromosuccinimide (117 mg, 0.66 mmol), 5-nitro-7-*anti*-trimethylsilylbicyclo[2.2.1]hept-2-ene (**2**)[13] (84:16 *endo*- to *exo*-nitro; 130 mg, 0.62 mmol) and methanol (3 ml) was stirred at room temperature for 14 h. After removal of the solvent under reduced pressure, water (5 ml) was added, and the mixture was extracted with diethyl ether (3 × 5 ml). The combined extracts were dried ($MgSO_4$) and evaporated under reduced pressure to give the bromonitronorbornene (**9**) as a chromatographically homogeneous straw-coloured solid (134 mg, quantitative). The loss of material on recrystallisation was large, but a sample was obtained for characterisation as colourless platelets, m.p. 69—70 °C (from hexane) (Found: C, 38.5; H, 3.7; N, 6.3. $C_7H_8BrNO_2$ requires C, 38.6; H, 3.7; N, 6.4%); $\nu_{max.}$(KBr) 1 523 and 1 365 (NO_2), and 735 cm^{-1}; δ($CDCl_3$) 6.36 (1 H, dd, *J* 6 and 3 Hz, 2-H), 6.11 (1 H, ddd, *J* 6, 3 and 0.6 Hz, 3-H), 4.55 (1 H, m, 7-H), 4.43 (1 H, ddd, *J* 9, 4, and 0.7 Hz, 5-H), 3.57 (1 H, br m, 4-H), 3.21 (1 H, br m, 1-H), 2.37 (1 H, dt, *J* 13.6 and 4 Hz, 6-H-*exo*), and 2.00 (1 H, ddd, *J* 13.6, 9 and 0.7 Hz, 6-H-*endo*). No molecular ion or other diagnostically useful peaks were apparent in the mass spectrum.

3-endo-*Nitro*-7-anti-*trimethylsilylbicyclo*[2.2.1]*hept*-5-*en*-2-exo-*ylmethanol* (**3**).—The *endo*-nitronorbornene (**12**) (3.0 g, 11.14 mmol) and lithium aluminium hydride (350 mg, 9.22 mmol) were stirred together at 0 °C in dry diethyl ether (75 ml) for 5 h and at room temperature for 2 h, after which the solvent was removed under reduced pressure. Dilute hydrochloric acid solution (2M; 25 ml) was added, and the resulting solution was extracted with diethyl ether (3 × 15 ml). The combined organic extracts were dried ($MgSO_4$) and evaporated under reduced pressure to an oil (2.56 g) which was chromatographed on silica gel using hexane–ethyl acetate mixtures as eluant. Some starting material (0.52 g, 17%) was recovered, as well as the desired exo-*methanol* (**3**) (1.09 g, 41%) as an oil which crystallised on seeding. A sample for characterisation was obtained as prisms, m.p. 61—63 °C (from hexane) (Found: C, 54.7; H, 7.8; N, 5.9. $C_{11}H_{19}NO_3Si$ requires C, 54.7; H, 7.9; N, 5.8%), R_F (hexane–ethyl acetate 3:1, v/v) 0.55; $\nu_{max.}$(KBr) 3 360br (OH), 1 550 and 1 380 (NO_2), and 1 255 and 850 cm^{-1} ($SiMe_3$); δ($CDCl_3$) 6.38 (1 H, dd, *J* 3.3 and 5.6 Hz, 6-H), 5.98 (1 H, dd, *J* 2.8 and 5.6 Hz, 5-H), 4.66 (1 H, t, *J* 3.7 Hz, 3-H), 3.77 (2 H, br d, *J* 7.4 Hz, CH_2O), 3.53 (1 H, br m, 4-H), 2.84 (1 H, br m, 1-H), 2.32 (1 H, dt, *J* 7.4 and 3.8 Hz, 2-H), 1.77 (1 H, br m, OH, exchanges with D_2O), 1.27 (1 H, s, 7-H), and −0.04 (9 H, s, $SiMe_3$); *m/z* 226 (13%, M^+ − Me), 138 (28), 123 (16), 105 (92), and 73 (100).

3-exo-*Nitro*-7-anti-*trimethylsilylbicyclo*[2.2.1]*hept*-5-*en*-2-endo-*ylmethanol* (**16**).—Compound (**16**) was prepared from the *endo*-ester (**15**) (1.01 g, 3.76 mmol) and lithium aluminium hydride (120 mg, 3.16 mmol) in dry diethyl ether (20 ml) at −22 °C for 0.75 h. Work-up and chromatography as above gave back starting material 0.46 g, 46%) and the endo-*methanol* (**16**) as a colourless oil (270 mg, 30%) which was purified by distillation at 125 °C/1 mmHg; R_F (diethyl ether) 0.75; $\nu_{max.}$(film) 3 390br (OH), 1 540 and 1 367 (NO_2), and 1 250 and 840 cm^{-1} ($SiMe_3$); δ($CDCl_3$) 6.20 (1 H, dd, *J* 6 and 3 Hz, 5-H), 6.09 (1 H, dd, *J* 6 and 3 Hz, 6-H), 4.01 (1 H, d, *J* 3.8 Hz, 3-H), 3.55 and 3.50 (3 H, d, *J* 7.6 Hz and m, CH_2O and 1-H), 3.05 (1 H, m, 4-H), 2.90 (1 H, m, 2-H), 1.61 (2 H, m, 7-H and OH), and −0.22 (9 H, s, $SiMe_3$) (Found: M^+ − Me, 226.089 98. $C_{10}H_{16}NO_3Si$ requires 226.089 95); *m/z* 226 (7%, M^+ − Me), 138 (14), 105 (84), and 73 (100).

Bromination of the exo-*Methanol* (**3**).—*N*-Bromosuccinimide (564 mg, 3.17 mmol) and the *exo*-methanol (**3**) (700 mg, 2.90 mmol) were stirred at room temperature in dry methanol (20 ml) for 24 h, after which the solvent was removed under reduced pressure. The resulting orange oil was separated by column chromatography on silica gel, using hexane–ethyl acetate mixtures as eluant, into three components: 7-anti-*bromo*-3-exo-*nitrobicyclo*[2.2.1]*hept*-5-*en*-2-endo-*ylmethanol* (**10**) (336 mg, 47%), m.p. 81—83 °C (from di-isopropyl ether) (Found: C, 38.7; H, 4.0; N, 5.6. $C_8H_{10}BrNO_3$ requires C, 38.7; H, 4.1; N, 5.7%), R_F (hexane–ethyl acetate 3:1, v/v) 0.18; $\nu_{max.}$(KBr) 3 340 (OH), and 1 533 and 1 374 cm^{-1} (NO_2); δ($CDCl_3$) 6.26 (2 H, m, 5-H and 6-H), 4.60 (1 H, s, 7-H), 4.06 (1 H, d, *J* 4.2 Hz, 3-H), 3.59 (1 H, m, 1-H or 4-H), 3.58 (2 H, d, *J* 7.4 Hz, CH_2O), 3.24 (1 H, m, 1-H or 4-H), 2.88 (1 H, m, 2-H), and 1.81 (1 H, br m, OH, exchanges with D_2O); *m/z* 201/203 (5%, M^+ − NO_2), 168 (8, M^+ − Br), 144/146 (19), and 65 (100); (5R*,7R*,9R*)-7-*bromo*-5-*nitro*-9-*trimethylsilyl*-2-*oxatricyclo*[4.2.1.$0^{4,8}$]*nonane* (**11**) (343 mg, 37%), m.p. 91—92.5 °C (from hexane) (Found: C, 41.2; H, 5.7; N, 4.4. $C_{11}H_{18}BrNO_3Si$ requires C, 41.3; H, 5.7; N, 4.4%), R_F (hexane–ethyl acetate 3:1, v/v) 0.54; $\nu_{max.}$(KBr) 1 534 and

1 358 (NO_2), 1 237, 855, and 835 cm^{-1} ($SiMe_3$); δ($CDCl_3$) 4.75 (1 H, m, 1-H), 4.30 (2 H, m, 7-H and 6-H), 4.16 (1 H, dd, *J* 9 and 5.6 Hz, 3-H-*endo*), 3.93 (1 H, d, *J* 9 Hz, 3-H-*exo*), 3.25 (1 H, m, 4-H), 3.05 (1 H, m, 8-H), 2.98 (1 H, m, 5-H), 0.54 (1 H, t, *J* 1.5 Hz, 9-H), and 0.20 (9 H, s, $SiMe_3$); *m/z* 304/306 (0.5%, M^+ − Me), 273/275 (1, M^+ − NO_2), 195 (18), and 73 (100).

Bromination of the endo-*Methanol* (**16**).—*N*-Bromosuccinimide (121 mg, 0.68 mmol) and the *endo*-methanol (**16**) (135 mg, 0.56 mmol) were stirred at room temperature in dry methanol (5 ml) for 12 h, after which the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel eluting with ethyl acetate–hexane mixtures, yielding (5R*,7R*,9R*)-9-*bromo*-5-*nitro*-7-*trimethylsilyl*-2-*oxatricyclo*[4.2.1.0^{4,8}]*nonane* (**19**) (170 mg, 95%). A sample, after several recrystallisations from cyclohexane followed by sublimation, was obtained as prisms, m.p. 116—117 °C (Found: C, 41.8; H, 5.8; N, 4.4. $C_{11}H_{18}BrNO_3Si$ requires C, 41.3; H, 5.7; N, 4.4%), R_F (hexane–ethyl acetate 3:1, v/v) 0.74; $\nu_{max.}$(KBr) 1 549 and 1 372 (NO_2), and 1 250, 890, and 837 cm^{-1} ($SiMe_3$); δ($CDCl_3$) 4.58 (1 H, d, *J* 4.4 Hz, 1-H), 4.20 (1 H, br s, 5-H), 3.94 (2 H, d, *J* 4.4 Hz, OCH_2), 3.46 (1 H, d, *J* 1.8 Hz, 9-H), 3.22 (2 H, m, 4-H and 6-H), 2.91 (1 H, m, 8-H), 1.49 (1 H, br s, 7-H), and 0.19 (9 H, s, $SiMe_3$); *m/z* 304/306 (5%, M^+ − Me), 91 (90), and 73 (100).

Crystallographic Analysis of the Tricycle (**11**).—$C_{11}H_{18}BrNO_3Si$, *M* = 320.27. Triclinic, *a* = 6.70(1), *b* = 9.70(1), *c* = 11.36(1) Å, α = 93.31(5), β = 94.57(5), γ = 105.68(5)°, *V* = 705.7 Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, λ = 0.710 7 Å), D_m (flotation) = 1.51 g cm^{-3}, *Z* = 2, D_x = 1.51 g cm^{-3}, *F*(000) = 328, space group $P\bar{1}$. Colourless prisms (by diffusion of hexane vapour into a solution of the compound in tetrachloromethane), 0.4 × 0.4 × 0.4 mm, μ(Mo-K_α) = 29.06 cm^{-1}.

Data collection and processing: Philips PW1100 four-circle diffractometer, scan mode, ω/2θ, scan width 1.5θ°, scan speed 0.05θ° s^{-1}, graphite-monochromated Mo-K_α radiation; 1 939 unique reflections measured ($3 < \theta < 23°$, $\pm h$, $\pm k$, l), 1 905 with $F_{obs} > \sigma F$. Stability of standard reflections *ca.* 3%. Intensity measurements were performed at room temperature. The data were corrected for Lorentz and polarisation effects, but not for absorption.

Structure analysis and refinement. The positions of the bromine atoms were determined from a Patterson map; subsequent difference Fourier maps and cycles of full-matrix least-squares refinement revealed the positions of the rest of the atoms. All non-hydrogen atoms were refined anisotropically; the hydrogen atoms were refined independently, with an overall isotropic temperature factor of 0.050(7) Å^{-2}. Unit weights were used throughout. At the termination of refinement, *R* was found to be 0.0522 for 1 905 reflections. The programme SHELX[14] was used on a CDC Cyber 750 machine for all crystallographic computations.

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