The Action of Sodium Nitrite–Acetic Acid on α- and β-Pinene. Participation by a Neighbouring Geminal Dinitro Group in the Base-catalysed Epimerization of a Secondary Alcohol

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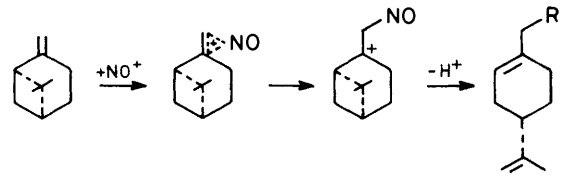
The reaction of (−)-α-pinene (1) with sodium nitrite–acetic acid gave principally (2*S*,4*R*)-2-nitromentha-1(6),8-diene (2) and smaller amounts of (2*S*,4*R*)-2-nitromenth-1(6)-en-8-yl acetate (3), (1*R*,4*S*)-2-*endo*-nitrato-6-*endo*-nitrobornane (4), (1*S*,4*R*)-3,3-dimethyl-2-*endo*-nitrato-6-*exo*-nitro-8,9-dinorbornane (5), and (−)-3-nitropin-2-ene (6). A similar reaction with (−)-β-pinene (8) afforded (4*S*)-7-nitromentha-1,8-diene (9) as the major product and (4*S*)-7-nitromenth-1-en-8-yl acetate (10), (1*S*,4*S*)-2-*endo*-nitrato-10-nitrobornane (11), and (1*R*,4*S*)-3,3-dimethyl-2-*endo*-nitrato-10-nitro-8,9-dinorbornane (12) in lower yields. Treatment of the nitro-nitrates (11) and (12) in basic medium gave the corresponding 10,10-dinitro alcohols (20) and (21) by intramolecular transfer of the nitro group with retention of configuration at C-2. In stronger alkaline conditions the dinitro *endo*-alcohol (21) produced unexpectedly the epimeric *exo*-alcohol (22). The neighbouring participation of the 10,10-dinitro group is shown to be essential for the epimerization to take place. Plausible mechanisms for these reactions are proposed.

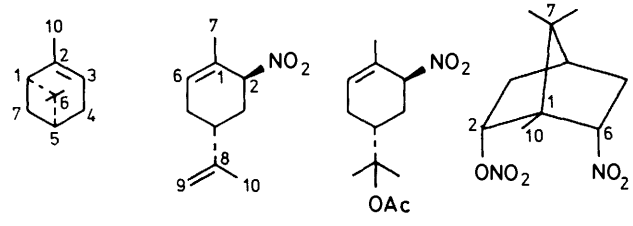
Continuing our studies on the reaction of nitrous acid with olefins, as a method for nitroimine synthesis,[1] we have investigated the action of this acid on α- and β-pinene as a route to nitrogenated *p*-menthane derivatives.

Since the last century it has been known [2] that β-pinene reacts, by a radical process, with N_2O_3, generated *in situ* in a two phase system by addition of acid to aqueous sodium nitrite, to give 2-nitroso-10-nitropinane (' β-pinene nitrosite ') whose pinene skeleton remains unmodified. To our knowledge α-pinene has not been subjected to the action of nitrogen oxides, and nitrosation of α-pinene has been accomplished with nitrosyl chloride [3] to yield 2-chloro-3-nitropinene dimer (' pinene nitrosochloride ') where the pinane skeleton was also unaltered. Although the mechanism for the addition of nitrosyl chloride is a controversial matter,[4] the result in the α-pinene case is better accommodated by a radical process. We were particularly interested in carrying out an ionic nitrosation, with sodium nitrite in acetic acid, of the pinene double bond in order to promote eventually the rearrangement of the pinene skeleton to menthane, as shown in Scheme 1 for β-pinene where R is expected to be a nitroso, nitro, or nitroimine group.

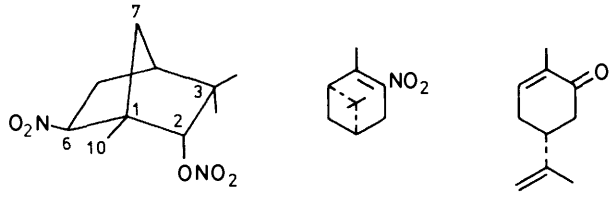
We report here the results obtained during the ionic nitrosation of α- and β-pinene.



Scheme 1.



(1) (2) (3) (4)



(5) (6) (7)

Results and Discussion

Ionic Nitrosation of (−)-α-*Pinene* (1).—The reaction of (−)-α-pinene (1) in dichloromethane–acetic acid (6 : 4) with excess of sodium nitrite at ambient temperature for 20 h, gave the nitromenthene (2) as the major product (35%) and smaller yields of compounds (3) (6%), (4) (8%), (5) (5%), and (6) (7%).

The high resolution mass spectrum of the nitro-*p*-menthane derivative (2) pointed to the molecular formula $C_{10}H_{15}NO_2$, the i.r. and ^1H and ^{13}C n.m.r. data (see Table 1 and Experimental section) being in agreement with the proposed structure. The pseudo-axial configuration of the nitro group at C-2 could be inferred from the shape of the signal of its geminal proton in the ^1H n.m.r. spectrum, a narrow multiplet at δ 4.90 ($W_{\frac{1}{2}}$ 11 Hz). We obtained chemical support for the structure (2) from the transformation of the nitronate derivative of (2) into (−)-carvone (7), *via* buffered titanium trichloride reduction.[5]

Compound (3) is closely related structurally to the above mentioned nitromenthane (2), as could be deduced from the spectroscopic data (see Table 1 and Experimental section). The conjugated nitro compound (6) was the only product with an unchanged pinane framework. It displayed a u.v. absorption at $\lambda_{max.}$ 285 nm and characteristic N=O stretching bands in the i.r. spectrum attributable to a vinylic nitro group.[6]

Table 1. ^{1}H N.m.r. data of menthane derivatives. δ Values for solutions in $CDCl_3$ (*J*/Hz or $W_{\frac{1}{2}}$/Hz in parentheses)

Compound	2-H	6-H	7-H	9-H	10-H	OAc
(2)	4.90 (m, 11)	6.0 (m, 11)	1.77 (br s)	4.85, 4.80 (2 × br s)	1.80 (d, 3)	
(3)	4.92 (m, 11)	5.98 (m, 11)	1.83 (br s, 5)	1.50 (s)	1.50 (s)	1.97 (s)
(9)	6.0 (m, 9)		4.82 (br s, 4)	4.73 (br s, 4)	1.72 (d, 2)	
(10)	5.98 (m, 9)		4.84 (br s, 4)	1.46 [a] (s)	1.43 [a] (s)	1.97 (s)

[a] Assignments may be reversed.

Table 2. ^{1}H N.m.r. data of bornane derivatives. δ Values for solutions in $CDCl_3$ (*J*/Hz or $W_{\frac{1}{2}}$/Hz in parentheses)

Compound	2-H	6-H	7-Me_2	10-H
(4)	5.36, 5.31 5.25, 5.21 (each d, 2)	4.71, 4.66 4.60, 4.55 (each d, 2)	1.05, 1.00 (each s)	1.39 (s)
(11)	5.63, 5.57 5.47, 5.41 (each d, 2)		1.03 (s)	4.49 (s)
(18)	5.17 (t, 7)		1.03, 0.94 (each s)	4.73, 4.28 (AB, 12)
(19)	4.28 (t, 7)		1.28, 0.83 (each s)	6.64 (s)
(20)	4.94, 4.84 (each m, 7)		1.03, 0.96 (each s)	6.38 (s)

Table 3. ^{1}H N.m.r. data of fenchane derivatives. δ Values for solutions in $CDCl_3$ (*J*/Hz or $W_{\frac{1}{2}}$/Hz in parentheses)

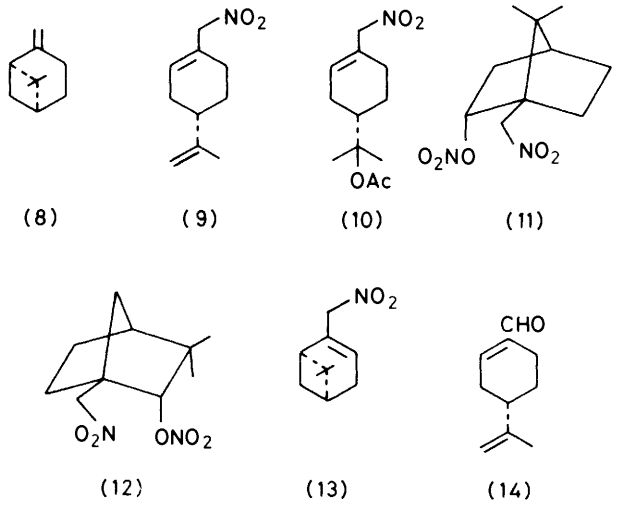
Compound	2-H	3-Me_2	6-H	10-H
(5)	4.68 (s)	1.22, 0.92 (each s)	4.85 (t, 7)	1.27 (s)
(12)	4.83 (d, 1.7)	1.18, 0.93 (each s)		4.58, 4.48 (AB, 12)
(21)	3.60 (br s, 5) [a]	1.05, 1.02 (each s)		6.71 (s)
(22)	3.81 (br s, 4.5) [a]	1.04, 0.91 (each s)		6.41 (s)
(23)		1.18, 1.11 (each s)		6.56 (s)
(24)	3.33 (br s, 5) [a]	1.00 (s)		4.86, 4.39 (AB, 12)

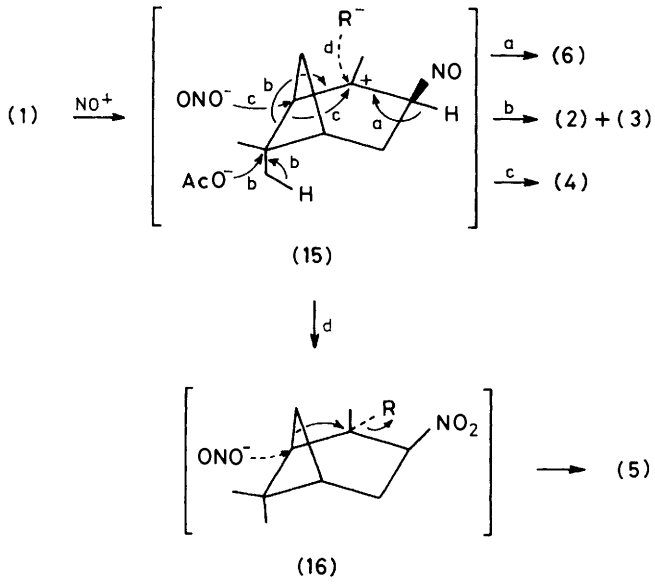
[a] After addition of D_2O.

The last two compounds isolated from the reaction of α-pinene with nitrous acid are the nitro-nitrates (4) and (5). Both have the same molecular formula, $C_{10}H_{16}N_2O_5$ (chemical ionization and high resolution mass spectrometry), and the presence of nitro and nitrate functions were clearly deduced from their i.r. spectra.[7] A detailed analysis of the ^{1}H n.m.r. spectra of these compounds (see Tables 2 and 3) led us unequivocally to ascribe bornane and fenchane (3,3-dimethyl-8,9-dinorbornane) frameworks for compounds (4) and (5) respectively. The 2-*endo*, 6-*endo* stereochemistry of the nitrate and nitro groups in the bornane (4) are deduced from the observed characteristic splitting patterns[8] for the C-2 and C-6 *exo*-geminal protons in the ^{1}H n.m.r. spectrum, which appear as the X part of an ABX system, with an additional long range coupling between both protons through four bonds. The pseudo-triplet due to 6-H in the ^{1}H n.m.r. spectrum of compound (5) indicates an *exo* disposition of the nitro group. Furthermore, a sharp singlet at δ 4.68 for the 2-H methine proton, which precludes long range coupling, allowed us to establish *endo* stereochemistry for the nitrate group.[8,9] It is difficult to exclude the regioisomeric arrangement of the nitro and nitrate functions in compounds (4) and (5) on the basis of the ^{1}H n.m.r. spectroscopic data. However, such structures would not be consistent with mechanistic and chemical considerations (see later).

Ionic Nitrosation of (−)-β-*Pinene* (8).—The reaction of the β-pinene (8) with sodium nitrite in acetic acid was performed as described for α-pinene; the β-pinene reacted faster, and the reaction was complete in 5 h at 0 °C. The reaction mixture was resolved by column chromatography, yielding the nitro compounds (9) (35%), (10) (5%), (11) (5%), and (12) (13%). A small amount of a substance that could not be totally purified and that seems to be, from the ^{1}H n.m.r. data, 10-nitropin-2-ene (13) was also obtained.

The structures of compounds (9)—(12) were established by spectroscopic means (see Tables and Experimental section) and by comparison with the α-pinene derivatives already discussed. In addition, the structure of the nitro compound (9) was established chemically by its reduction[5] with titanium tetrachloride into (−)-perillaldehyde (14). The shape of the signal due to 2-H in the ^{1}H n.m.r. spectrum of the nitro-





Scheme 2.

nitrato-bornane (11) (see Table 2) indicates unambiguously the *endo* stereochemistry of the C-2 nitrate group.[8] The stereochemistry of the 2-nitrate group in the fenchane derivative (12) could not be deduced from the ^{1}H n.m.r. evidence, inasmuch as the same doublet (J 2 Hz) for 2-H would be expected for both stereoisomers as a consequence of long range couplings.[9] However, only the *endo* stereochemistry is compatible with mechanistic considerations (*cf.* the proposed reaction mechanism in Scheme 2). This *endo*-disposition of the C-2 functional group is always obtained in related pinane ⟶ fenchane transformations;[9,10] in some cases X-ray crystal structure analyses have been carried out.[11]

The production of optically pure (−)-carvone (7) and (−)-perillaldehyde (14) from the nitromenthenes (2) and (9), respectively, indicates that a carbon rearrangement takes place in a concerted manner. The mechanism outlined in Scheme 2 is a plausible explanation for the formation of compounds (2)—(6) in the ionic nitrosation of α-pinene. The initially formed nitroso and nitrite esters were not isolated; in every case they underwent oxidation under the reaction conditions to the nitro and nitrate esters, respectively. It seems reasonable to assume that the nitrato-fenchane (5) arose from a double inversion of configuration at C-2 [9] *via* the intermediates (15) and (16) in which R could be OAc, ONO, or ONO_2 (path d).

The reasons why the only external nucleophile which is effective for the pinane ⟶ menthane transposition (1) ⟶ (3) is the acetate anion, while in the pinane ⟶ bornane and fenchane (1) ⟶ (4), (5) it is the nitrite anion, are not yet clear.

Basic Treatment of the Nitro-nitrates: Participation of the Neighbouring Dinitro Group in the Base-catalysed Epimerization of a Secondary Alcohol.—It has been reported by T. E. Stevens [12] that the nitro-nitrate * (18), obtained by treatment of (±)-camphene (17) with dinitrogen pentaoxide, undergoes base-catalysed intramolecular migration of the NO_2 group of the C-2 nitrate to C-10 to afford the dinitro alcohol (19). As the stereochemical behaviour of this interesting reaction was not established by the author we have been prompted to examine its scope in more detail. Furthermore, this internal displacement applied to the nitro-nitrates, obtained by us in the nitrosation of pinenes, can supply additional chemical support to the proposed structures.

The reaction of *endo*- and *exo*-nitrato-nitrobornanes (11) and (18) with methanolic potassium hydroxide gave after acidification, the 10,10-dinitro compounds (20) and (19), respectively. The structures of these products can be easily deduced from their spectroscopic data. Their i.r. spectra lack nitrate bands, but absorptions indicative of hydroxy and nitro groups are observed. In their ^{1}H n.m.r. spectra, 2-H is observed as a triplet in compound (19) (*endo*-H) and as two multiplets in (20) (*exo*-H).

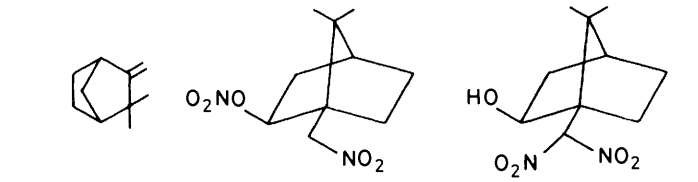
The above mentioned results indicate that both *exo*- and *endo*-nitrates undergo base-catalysed rearrangements with retention of configuration at C-2. In the same way, mildly basic treatment (2% KOH–MeOH, 25 °C, 30 min) of the fenchane derivative (12) afforded, in high yield, the dinitro-alcohol (21) in which the *endo* disposition of the hydroxy group is assigned on the basis of the retention of configuration observed in the bornane series. These intramolecular migrations exclude the regioisomeric disposition, compatible with the spectroscopic data, of the nitro and nitrate functions in (11) and (12).

Treatment of the dinitro alcohol (21) in stronger alkaline conditions (4% KOH–MeOH, 60 °C, 5 h) produced, unexpectedly, the epimeric *exo*-alcohol (22) in 80% yield. The fact that both compounds yielded the ketone (23) by buffered pyridinium chlorochromate oxidation demonstrated that (21) and (22) only differ in the stereochemistry of the C-2 hydroxy groups.

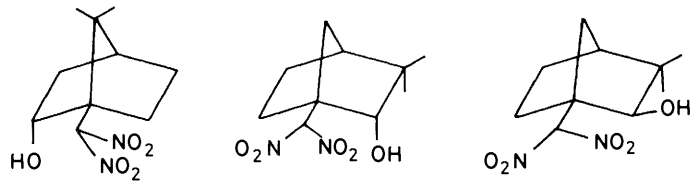
We could explain this remarkable mild base-catalysed epimerization of the C-2 hydroxy group only by considering the participation of the neighbouring geminal nitro groups at C-10.[13] In Scheme 3 we describe a feasible mechanism for this reaction. A set of experiments was performed in order to substantiate this hypothesis.

As expected, a structurally induced epimerization was excluded as the *endo*-hydroxyfenchane (25) was unaltered after treatment for 22 h with 4% KOH–MeOH at 60 °C. To test the possibility that the isomerization could be assisted by one nitro group we prepared the mononitro alcohol (24) by catalytic hydrogenation [14] or reduction with tri-n-butyltin hydride of (18). The different alkaline treatments, carried out in an attempt to epimerize the alcohol group in (24) were

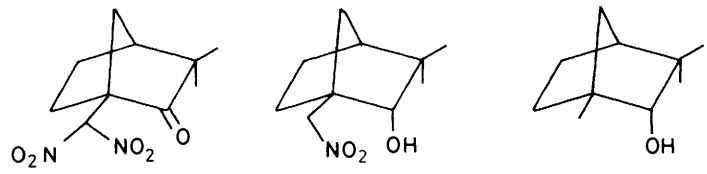
* As the author gave no information on the stereochemistry at C-2, we have prepared compound (18) and established by ^{1}H n.m.r. (see Table 2) the *exo*-disposition of the nitrate group, as expected from mechanistic considerations.



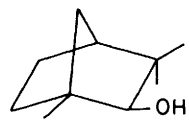
(17) (18)[a] (19)[a]



(20) (21) (22)



(23) (24) (25)



(26)

[a] Racemic compound, only one enantiomer shown

unsuccessful. Treatment of compound (21) with 4% NaOMe–MeOH at 60 °C for 20 h gave only starting material. This seems to rule out an alternative mechanism involving a reverse Aldol reaction with cleavage of the C(1)–C(2) bond and subsequent recombination.

In order to examine this uncommon reaction further, and particularly its scope, we attempted the epimerization of the structurally related dinitrobornane (20). Compound (20) was recovered unchanged after alkaline treatment with 4% KOH–MeOH at 60 °C for 22 h, and no epimeric alcohol (19) could be detected. The same result was obtained with the *exo*-alcohol (19) after several attempts at epimerization under the same conditions. The non-interconversion of the isomeric alcohols (19) and (20) can be explained if we take into account the steric effect of the bornane skeleton [15] which impedes the eventual approach of the solvated hydroxy anion to either of the faces in an intermediate such as (27).

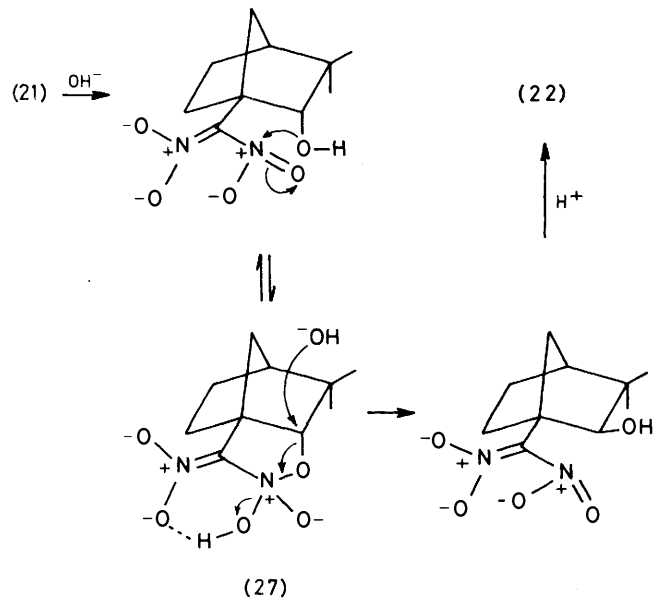
The epimerization of alcoholic functions catalysed by base *via* a reversible redox process is known [16] but to our knowledge this is the first reported case where a dinitro group participates like the neighbouring group in the base-catalysed inversion of an alcohol.

Other examples of this reaction are currently under investigation.

Experimental

M.p.s were determined with a Kofler hot-stage apparatus and are uncorrected. Optical rotations were measured for solutions in $CHCl_3$. ^1H N.m.r. spectra were recorded with a Perkin-Elmer R-12B (60 MHz), a R-32 (90 MHz), or a Bruker WP200SY (200 MHz) instrument and ^{13}C n.m.r. spectra on a Varian C.F.T.-20 (20 MHz) instrument for solutions in $CDCl_3$ with Me_4Si as internal reference. I.r. spectra were measured on a Perkin-Elmer 257 instrument in $CHCl_3$ (unless otherwise stated) and u.v. spectra on a Perkin-Elmer 402 spectrophotometer. Low- and high-resolution, and chemical ionization (CH_4) mass spectra were determined with a VG Micromass ZAB-2F spectrometer. Thin-layer chromatography (t.l.c.) was performed on Merck silica gel 60 and column chromatography on Merck silica gel (0.063—0.2 mm). The spray reagent for t.l.c. was vanillin (1 g) in H_2SO_4–EtOH (4 : 1; 200 ml), or I_2.

Reaction of (−)-α-*Pinene* (1) *with Nitrous Acid.*—To a cold (0 °C) solution of α-pinene (1) (29.6 g) in methylene dichloride (400 ml) and glacial acetic acid (270 ml), sodium nitrite (130 g) was added in portions with vigorous stirring during 6 h, and the stirring continued for 14 h at ambient temperature. After the addition of ice–water, the solution was extracted with methylene dichloride and the organic phase was washed with aqueous potassium hydroxide and water, dried (Na_2SO_4), and evaporated under reduced pressure, to give a dark oil (40 g). This residue yielded, after several column chromatographies (benzene–n-hexane mixtures as eluant), starting material (10.0 g), (2S,4R)-2-*nitromentha*-1(6),8-*diene* (2) (9.1 g), (2S,4R)-2-*nitromenth*-1(6)-*en*-8-*yl acetate* (3) (2.0 g), (1R,4S)-2-endo-*nitrato*-6-endo-*nitrobornane* (4) (2.8 g), and a mixture



Scheme 3.

(4.5 g) of (1S,4R)-3,3-*dimethyl*-2-endo-*nitrato*-6-exo-*nitro*-8,9-*dinorbornane* (5) and (−)-3-*nitropin*-2-*ene* (6). Compound (6) (1.8 g) was separated from this mixture by bulb-to-bulb distillation (50 °C, 0.02 mmHg) and the residue was crystallized from n-hexane to give compound (5) (1.7 g).

Compound (2) was purified by Kugelrohr distillation (50 °C, 0.05 mmHg); $[\alpha]_D$ −140° (*c*, 0.3); *m/z* 181.1106 (1%, $C_{10}H_{15}NO_2$ = 181.1102, M^+), 135.1190 (30, $C_{10}H_{15}$ = 135.1174, $M^+ - NO_2$), 134.1103 (15, $C_{10}H_{14}$ = 134.1095, $M^+ - NO_2H$), 107.0878 (60, C_8H_{11} = 107.0861), 93.0712 (100, C_7H_9 = 93.0705), and 91.0554 (50, C_7H_7 = 91.0548); $\nu_{max.}$ 3 080, 3 020, 1 640, 900, 850 (C=C), 1 540, and 1 370 cm^{-1} (NO_2); δ_C 147.35 (C-8), 131.3 (C-6), 126.3 (C-1), 110.0 (C-9), 85.8 (C-2), 35.3 (C-4), 32.8 (C-3), 30.5 (C-5), 21.0 (C-7 or -10), and 20.8 p.p.m. (C-10 or -7).

Compound (3) was chromatographed by column chromatography (benzene as eluant) to give an oil which could not be distilled; $[\alpha]_D$ −132° (*c*, 0.22); *m/z* 241 (0.1%, M^+), 195.1393 (0.7, $C_{12}H_{19}O_2$ = 195.1385, $M^+ - NO_2$), 182.1206 (0.5, $C_{10}H_{16}NO_2$ = 182.1181, $M^+ - AcO$), 151.1121 (4, $C_{10}H_{15}O$ = 151.1123), 135.1180 (90, $C_{10}H_{15}$ = 135.1173, $M^+ - NO_2 - AcOH$), 119.0842 (20, C_9H_{11} = 119.0860), 107.0861 (35, C_8H_{11} = 107.0861), 93.0695 (100, C_7H_9 = 93.0705), and 91.0546 (35, C_7H_7 = 91.0548); $\nu_{max.}$ 3 020 (C=C), 1 725 and 1 240 (OAc), 1 540, and 1 370 cm^{-1} (NO_2).

Compound (4) was crystallized from n-hexane, m.p. 138—141 °C; $[\alpha]_D$ 0° (*c*, 0.24); *m/z* 245 (c.i., $M^+ + 1$), 197.1060 (6%, $C_{10}H_{15}NO_3$ = 197.1052, $M^+ - NO_2H$), 182.0817 (15, $C_9H_{12}NO_3$ = 182.0817, $M^+ - NO_2H - Me$), 153.0936 (50, $C_9H_{13}O_2$ = 153.0915), 152.1207 (20, $C_{10}H_{16}O$ = 152.1201, $M^+ - 2\ NO_2$), 151.1130 (16, $C_{10}H_{15}O$ = 151.1122, $M^+ - NO_2H - NO_2$), 137.0997 (65, $C_9H_{13}O$ = 137.0967, $M^+ - 2\ NO_2 - Me$), 135.1156 (50, $C_{10}H_{15}$ = 135.1174), 108.0939 (100, C_8H_{12} = 108.0939), and 107.0868 (100, C_8H_{11} = 107.0861); $\nu_{max.}$ 1 640, 1 280, 850 (ONO_2), 1 550, and 1 370 cm^{-1} (NO_2).

Compound (5) was crystallized from n-hexane, m.p. 68—70 °C; $[\alpha]_D$ +109° (*c*, 0.2); *m/z* 245 (c.i., $M^+ + 1$), 198 (5%, $M^+ - NO_2$), 182.1186 (2, $C_{10}H_{16}NO_2$ = 182.1180, $M^+ - ONO_2$), 151.1123 (30, $C_{10}H_{15}O$ = 151.1122), 135.1125 (20, $C_{10}H_{15}$ = 135.1173), and 107.0859 (100, C_8H_{12} = 107.0860); $\nu_{max.}$ 1 640, 1 280, 850 (ONO_2), 1 560, and 1 370 cm^{-1} (NO_2).

Compound (6) was purified by Kugelrohr distillation (50 °C, 0.03 mmHg); $[\alpha]_D$ −61° (*c*, 0.2); *m/z* 181.1108 (3%, $C_{10}H_{15}NO_2$ = 181.1102, M^+), 164.1085 (5, $C_{10}H_{14}NO$ = 164.1075, $M^+ - OH$), 139.0629 (20, $C_7H_9NO_2$ = 139.0633), 134.1077 (10, $C_{10}H_{14}$ = 134.1096, $M^+ - NO_2H$), 122.0607 (40, C_7H_8NO = 122.0606), 119.0856 (40, C_9H_{11} = 119.0861), 93.0377 (35, C_7H_9 = 93.0704), 92.0594 (100, C_7H_8 = 92.0626), and 91.0532 (60, C_7H_7 = 91.0548); $\nu_{max.}$ 1 640 (C=C), 1 490, and 1 330 cm^{-1} (NO_2); $\lambda_{max.}$ (EtOH) 285 nm (ε 6 000); δ_H 2.33 (3 H, br s, $W_{\frac{1}{2}}$ 6 Hz, 2-Me), 1.34, and 0.86 (total 6 H, each s, 6-Me_2).

(−)-*Carvone* (p-*Mentha*-6,8-*dien*-2-*one*) (7) *from* (2S,4R)-2-*Nitromentha*-1(6),8-*diene* (2).—The nitro compound (2) (0.5 g) was dissolved in methanol (7 ml) and treated with sodium methoxide (0.18 g) in methanol (7 ml) at 0 °C under argon. Buffered $TiCl_3$–NH_4OAc (28.3 ml) [prepared by addition of NH_4OAc (9.92 g) in water (38.35 ml) to 24% aqueous $TiCl_3$ (11.28 g) under argon] was then added in one portion to the nitronate solution at 0 °C. The reaction mixture was stirred at ambient temperature for 2 h and then poured into a mixture of diethyl ether and aqueous hydrochloric acid (5%). The aqueous phase was extracted several times with ether; the organic extracts were combined, washed three times with water, dried (Na_2SO_4), and evaporated to dryness under reduced pressure. Column chromatography of the residue (benzene–n-hexane, 7 : 3, as eluant) gave (−)-carvone (7) (0.18 g), b.p. 85 °C at 4 mmHg; $[\alpha]_D$ −43° (*c*, 0.26) {an authentic sample of (−)-carvone gave b.p. 100 °C at 10 mmHg, $[\alpha]_D$ −48° (*c*, 0.24)}; *m/z* 150 (7%, M^+), 135 (3), 108 (21), 82 (66), and 78 (100); $\nu_{max.}$ 3 060, 1 655, and 900 cm^{-1}; δ_H 6.82 (1 H, m, $W_{\frac{1}{2}}$ 12 Hz, 6-H), 4.84 (2 H, m, $W_{\frac{1}{2}}$ 9 Hz, 9-H_2), and 1.78 (6 H, br s, $W_{\frac{1}{2}}$ 8 Hz, 1-Me and 8-Me). The compound (7) was identical (i.r., ^1H n.m.r., and mass spectra, t.l.c.) with an authentic reference sample.

Reaction of (−)-β-*Pinene* (8) *with Nitrous Acid.*—To a cold (0 °C) solution of β-pinene (8) (27 g) in methylene dichloride (500 ml) and glacial acetic acid (200 ml), sodium nitrite (147 g) was added in portions with vigorous stirring during 5 h. After additional stirring for 0.5 h, the reaction was worked up as previously described for the nitrous acid treatment of (−)-α-pinene (1). The residue (42 g), after several column chromatographies (benzene–n-hexane mixtures as eluant) yielded (4S)-7-*nitromentha*-1,8-*diene* (9) (12.6 g), (4S)-7-*nitromenth*-1-*en*-8-*yl acetate* (10) (2.4 g), (1S,4S)-2-endo-*nitrato*-10-*nitrobornane* (11) (2.4 g), (1R,4S)-3,3-*dimethyl*-2-endo-*nitrato*-10-*nitro*-8,9-*dinorbornane* (12) (6.3 g), and 10-*nitropin*-2-*ene* (13) (0.05 g).

Compound (9) was purified by Kugelrohr distillation (60 °C, 0.1 mmHg); $[\alpha]_D$ −67° (*c*, 0.25); *m/z* 182 (c.i., $M^+ + 1$), 164.1080 (10%, $C_{10}H_{14}NO$ = 164.1075, $M^+ - OH$), 135.1163 (100, $C_{10}H_{15}$ = 135.1173, $M^+ - NO_2$), 133.1025 (60, $C_{10}H_{13}$ = 133.1017), 107.0839 (100, C_8H_{11} = 107.0861), 105.0697 (40, C_8H_9 = 105.0704), and 93.0691 (100, C_7H_9 = 93.0704); $\nu_{max.}$ 3 070, 3 020, 1 640, 895 (C=C), 1 550, and 1 375 cm^{-1} (NO_2); δ_C 148.8 (C-8), 132.8 (C-2), 128.3 (C-1), 109.25 (C-9), 82.35 (C-7), 40.2 (C-4), 30.8 (C-3), 27.1 (C-6 or -5), 27.0 (C-5 or -6), an 20.7 p.p.m. (C-10).

Compound (10) was purified by Kugelrohr distillation (90 °C, 0.01 mmHg); $[\alpha]_D$ −61° (*c*, 0.23); *m/z* 242 (c.i., $M^+ + 1$), 195 (0.5%, $M^+ - NO_2$), 182.1160 (1, $C_{10}H_{16}NO_2$ = 182.1181, $M^+ - AcO$), 181.1101 (1, $C_{10}H_{15}NO_2$ = 181.1103, $M^+ - AcOH$), 151.1088 (3, $C_{10}H_{15}O$ = 151.1123), 135.1167 (100, $C_{10}H_{15}$ = 135.1174, $M^+ - NO_2 - AcOH$), 119.0854 (5, C_9H_{11} = 119.0860), 107.0848 (17, C_8H_{11} = 107.0860), 93.0706 (50, C_7H_9 = 93.0705), and 91.0542 (12, C_7H_7 =

91.0548); $\nu_{max.}$ 3 020 (C=C), 1 725, 1 250 (OAc), 1 545, and 1 370 cm^{-1} (NO_2).

Compound (11) was crystallized from n-hexane, m.p. 94—95 °C; $[\alpha]_D$ −64° (*c*, 0.24); *m/z* 245 (c.i., $M^+ + 1$), 198.1136 (0.5%, $C_{10}H_{16}NO_3 = 198.1130$, $M^+ - NO_2$), 180.1022 (2, $C_{10}H_{14}NO_2 = 180.1025$), 137.0968 (80, $C_9H_{13}O = 137.0966$), 135.1173 (20, $C_{10}H_{15} = 135.1174$), 108.0934 (100, $C_8H_{12} = 108.0939$), and 107.0868 (80, $C_8H_{11} = 107.0861$); $\nu_{max.}$ 1 640, 1 280, 855 (ONO_2), 1 550, and 1 380 cm^{-1} (NO_2).

Compound (12) was purified by Kugelrohr distillation (80 °C, 0.05 mmHg); $[\alpha]_D$ +34° (*c*, 0.23); *m/z* 245 (c.i., $M^+ + 1$), 198 (0.5%, $M^+ - NO_2$), 182 (2, $M^+ - ONO_2$), 152.1188 (15, $C_{10}H_{16}O = 152.1201$), 151.1123 (15, $C_{10}H_{15}O = 151.1123$), 137.0981 (55, $C_9H_{13}O = 137.0966$), 135.1166 (20, $C_{10}H_{15} = 135.1174$), 133.1018 (30, $C_{10}H_{13} = 133.1017$), and 107.0857 (100, $C_8H_{11} = 107.0861$); $\nu_{max.}$ 1 635, 1 280, 855 (ONO_2), 1 550, and 1 380 cm^{-1} (NO_2).

Compound (13), obtained in small quantities, could not be totally purified; δ_H 5.84 (1 H, m, $W_{\frac{1}{2}}$ 9 Hz, 3-H), 4.87 (2 H, br s, $W_{\frac{1}{2}}$ 4 Hz, 10-H_2), 1.31 and 0.82 (total 6 H, each s, 6-Me_2).

(−)-*Perillaldehyde* (p-*Mentha*-6,8-*dien*-7-*al*) (14) *from* (4S)-7-*Nitromentha*-1,8-*diene* (9).—The nitro compound (9) (0.6 g) in methanol (7 ml) was treated with sodium methoxide (0.19 g) in methanol (7 ml) and a buffered aqueous solution of $TiCl_3$–NH_4OAc (30 ml) as previously described for (−)-carvone (7) from compound (2). Column chromatography of the residue gave (−)-perillaldehyde (14) (0.28 g), b.p. 95—98 °C at 7 mmHg; $[\alpha]_D$ −121° (*c*, 0.27 in EtOH) {lit.,[17] b.p. 104—105 °C at 10 mmHg; $[\alpha]_D$ −121° (EtOH)}; *m/z* 150 (10%, M^+), 135 (8), 122 (10), 78 (100), and 68 (43); $\nu_{max.}$ 2 720, 1 665, and 1 640 cm^{-1}; δ_H 9.46 (1 H, s, 7-H), 6.86 (1 H, m, $W_{\frac{1}{2}}$ 10 Hz, 2-H), 4.80 (2 H, m, $W_{\frac{1}{2}}$ 9 Hz, 9-H_2), and 1.80 (3 H, br s, $W_{\frac{1}{2}}$ 5 Hz, 8-Me). Compound (14) was identical (i.r., ^1H n.m.r., and mass spectra, t.l.c.) with an authentic reference sample.

Reaction of (±)-*Camphene* (17) *with Dinitrogen Pentaoxide.*—A solution of camphene (17) (10 g) in methylene dichloride (150 ml) was cooled to −15 °C and dinitrogen pentaoxide [18] (9 g) in methylene dichloride (100 ml) was added during 15 min. The reaction mixture was allowed to warm to 3 °C and was stirred for an additional 15 min. Aqueous sodium hydrogen carbonate was then added to the reaction mixture and the organic phase was washed with water, dried (Na_2SO_4), and evaporated under reduced pressure to give an oil (15 g) which was chromatographed. Elution of the column with benzene–n-hexane (1 : 1) gave (±)-2-*exo*-nitrato-10-nitrobornane (18) (2 g), m.p. 99—100 °C (n-pentane) (lit.,[12] m.p. 98—99 °C); *m/z* 198 (c.i., $M^+ - NO_2$), 182 (5%, $M^+ - ONO_2$), 180 (1), 137 (100), 135 (25), 108 (50), and 107 (65); $\nu_{max.}$ 1 635, 1 280, 850 (ONO_2), 1 550, and 1 375 cm^{-1} (NO_2).

Reaction of (1S,4S)-2-endo-*Nitrato*-10-*nitrobornane* (11) *with Potassium Hydroxide.*—To a solution of the nitronitrate (11) (60 mg) in methanol (15 ml) containing water (2%), potassium hydroxide (1.0 g) in methanol (20 ml) was added, and the mixture was stirred at 60 °C for 3 h. After addition of water the mixture was acidified with aqueous hydrochloric acid, and extracted with methylene dichloride. The organic phase was washed three times, dried (Na_2SO_4), and evaporated under reduced pressure. Column chromatography of the crude mixture (benzene–ethyl acetate, 95 : 5 as eluant) gave starting material (11) (17 mg) and the *dinitro compound* (20) (22 mg), m.p. 110—130 °C (n-pentane);* $[\alpha]_D$ −60° (*c*, 0.16); *m/z* 243 (c.i., $M^+ - 1$), 227.1049 (30%, $C_{10}H_{15}N_2O_4 = 227.1032$, $M^+ - OH$), 198.1112 (15, $C_{10}H_{16}NO_3 = 198.1130$, $M^+ - NO_2$), 180.1013 (100, $C_{10}H_{14}NO_2 = 180.1024$, $M^+ - NO_2 - H_2O$), and 137.0935 (100, $C_9H_{13}O = 137.0966$); $\nu_{max.}$ 3 600 (OH), 1 575, and 1 320 cm^{-1} (NO_2).

Reaction of (±)-2-exo-*Nitrato*-10-*nitrobornane* (18) *with Potassium Hydroxide.*—The title compound (18) (0.1 g) was treated with 2% methanolic potassium hydroxide (46 ml) at 25 °C for 30 min. Work-up gave (±)-2-*exo*-hydroxy-10,10-dinitrobornane (19) (0.1 g), m.p. 130—159 °C (n-pentane) * (lit.,[12] 157—158 °C); *m/z* (c.i.) 243 (3%, $M^+ - 1$), 227 (5, $M^+ - OH$), 198 (3, $M^+ - NO_2$), 180 (100, $M^+ - NO_2 - H_2O$), 151 (7), 138 (15), and 137 (15); $\nu_{max.}$ (KBr) 3 580 (OH), 1 565, and 1 330 cm^{-1} (NO_2).

Reaction of (1R,4S)-3,3-*Dimethyl*-2-endo-*Nitrato*-10-*nitro*-8,9-*dinorbornane* (12) *with Potassium Hydroxide.*—The title product (12) (0.15 g) was treated with 4% methanolic potassium hydroxide (70 ml) at 60 °C for 1.5 h. Work-up and column chromatography (benzene–ethyl acetate, 95 : 5 as eluant) of the residue gave (1R,4S)-2-endo-*hydroxy*-3,3-*dimethyl*-10,10-*dinitro*-8,9-*dinorbornane* (21) (0.05 g) and (1R,4S)-2-exo-*hydroxy*-3,3-*dimethyl*-10,10-*dinitro*-8,9-*dinorbornane* (22) (0.085 g).

Compound (21) was crystallized from n-pentane, m.p. 68—69 °C; $[\alpha]_D$ +67° (*c*, 0.2); *m/z* (c.i.) 243 (3%, $M^+ - 1$), 227 (13, $M^+ - OH$), 198 (3, $M^+ - NO_2$), 182 (17), 181 (35), 180 (40, $M^+ - NO_2 - H_2O$), 151 (20), and 135 (100); $\nu_{max.}$ 3 610 (OH), 1 570, and 1 330 cm^{-1} (NO_2).

Compound (22) was crystallized from n-pentane, m.p. 70—71 °C; $[\alpha]_D$ +50° (*c*, 0.22); *m/z* (c.i.) 243 (60%, $M^+ - 1$), 227 (80, $M^+ - OH$), 198 (22, $M^+ - NO_2$), 182 (90), 181 (100), 180 (100, $M^+ - NO_2 - H_2O$), 151 (77), and 135 (90); $\nu_{max.}$ (KBr) 3 545 (OH), 1 570, and 1 330 cm^{-1} (NO_2).

Treatment of compound (12) with 2% methanolic potassium hydroxide at 25 °C for 30 min gave exclusively the dinitro compound (21) in 90% yield. Under these conditions the isomeric alcohol (22) was not detected.

Reaction of (1R,4S)-2-endo-*Hydroxy*-3,3-*dimethyl*-10,10-*dinitro*-8,9-*dinorbornane* (21) *with Potassium Hydroxide.*—The title compound (21) (45 mg) was treated with 4% methanolic potassium hydroxide (20 ml) at 60 °C for 5 h. Work-up and column chromatography (benzene–ethyl acetate, 95 : 5 as eluant) of the crude mixture gave starting material (4 mg) and the isomeric alcohol (22) (36 mg).

Reaction of (1R,4S)-2-endo-*Hydroxy*-3,3-*dimethyl*-10,10-*dinitro*-8,9-*dinorbornane* (21) *with Pyridinium Chlorochromate.*—To a solution of compound (21) (45 mg) in anhydrous methylene dichloride (15 ml) containing sodium acetate (24 mg), pyridinium chlorochromate (0.5 g) was added with stirring at ambient temperature. After 7 h the methylene dichloride suspension was decanted and the solid residue washed three times with ethyl acetate. The combined organic solutions were passed through a short pad of silica gel, (0.063—0.2 mm) and the solvent evaporated under reduced pressure. Column chromatography of the residue (benzene–ethyl acetate 95 : 5, as eluant) gave the *ketone* (23) (38 mg), m.p. 48—49 °C (n-pentane); $[\alpha]_D$ −83° (*c*, 0.2); *m/z* 243 (c.i., $M^+ + 1$), 196 (10%, $M^+ - NO_2$), 168 (100, $M^+ - NO_2 - CO$), 151 (65), 136 (75), and 134 (30); $\nu_{max.}$ 1 740 (C=O), 1 575, and 1 330 cm^{-1} (NO_2).

* In our hands the crystals softened and changed their form at 110 °C, melting finally at 130 °C. Similar behaviour was observed for the *exo*-isomer (19), which melts between 130—159 °C.

Reaction of (1R,4S)-2-exo-*Hydroxy*-3,3-*dimethyl*-10,10-*dinitro*-8,9-*dinorbornane* (22) *with Pyridinium Chlorochromate.*—A solution of compound (22) (60 mg) in methylene dichloride (15 ml) containing sodium acetate (24 mg), was treated with pyridinium chlorochromate (0.36 g), as described above for compound (21), to yield the ketone (23) (51 mg), identical with that obtained by oxidation of compound (21).

Reaction of (±)-2-exo-*Hydroxy*-10,10-*dinitrobornane* (19), (1S,4S)-2-endo-*Hydroxy*-10,10-*dinitrobornane* (20), (1R,4S)-2-exo-3,3-*Dimethyl*-10,10-*dinitro*-8,9-*dinorbornane* (22), *and* 2-endo-*Hydroxy*-3,3-*dimethyl*-8,9-*dinorbornane* (25) *with Potassium Hydroxide.*—Treatment of compounds (19), (20), (22), and (25) with 4% methanolic potassium hydroxide at 60 °C for 22 h gave only the corresponding starting materials. The respective isomeric alcohols (20), (19), (21), and (26) were not detected (t.l.c., ^{1}H n.m.r.).

Production of (1R,4S)-2-endo-*Hydroxy*-3,3-*dimethyl*-10-*nitro*-8,9-*dinorbornane* (24) *from* (1R,4S)-2-endo-*Hydroxy*-3,3-*dimethyl*-10,10-*dinitro*-8,9-*dinorbornane* (21).—(i) *By catalytic hydrogenation.* To a pre-reduced platinum(IV) oxide (40 mg) suspension in ethyl acetate (4 ml) the 10,10-dinitro compound (21) (95 mg) in ethyl acetate (5 ml) was added and the mixture was stirred under hydrogen at atmospheric pressure until four moles of hydrogen had been taken up (25 min). Subsequently, the catalyst was filtered off and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (benzene–ethyl acetate, 97 : 3 as eluant) to give (1R,4S)-2-endo-*hydroxy*-3,3-*dimethyl*-10-*nitro*-8,9-*dinorbornane* (24) (73 mg), m.p. 72—73 °C (n-pentane); $[\alpha]_D$ −15° (*c*, 0.13); *m/z* (c.i.) 200 (4%, $M^+ + 1$), 198 (16, $M^+ - 1$), 182 (90, $M^+ -$ OH), 153 (20), 151 (30), 136 (60), and 135 (100); $\nu_{max.}$ 3 610 (OH), 1 545, and 1 380 cm^{-1} (NO_2).

(ii) *With tri-n-butyltin hydride.* A solution of the 10,10-dinitro compound (21) (14 mg, 0.05 mmol) in dry benzene (2.5 ml) containing azobisisobutyronitrile (AIBN) (10 mg) was treated with tri-n-butyltin hydride (72 mg, 0.25 mmol) under argon at reflux temperature for 1 h. Column chromatography (benzene–ethyl acetate, 97 : 3, as eluant) of the crude product yielded compound (24) (10 mg), identical with that previously obtained by catalytic hydrogenation of (21).

Treatment of compound (24) with 2% methanolic potassium hydroxide at 25 °C for 24 h gave exclusively starting material. In stronger basic conditions (4% KOH–MeOH, 60 °C, 16 h) it gave a complex mixture in which the starting material was the major component.

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