Reactions of the Potassium Salt of 1,7,7-Trimethyl-*N*-nitrobicyclo[2.2.1]heptan-2-imine with Bromine and Nitrous Acid: Synthesis of 3-*exo*-Bromo-1,7,7-trimethyl-*N*-nitrobicyclo[2.2.1]heptan-2-imine, 3-*endo*-Bromo-1,7,7-trimethyl-*N*-nitrobicyclo[2.2.1]heptan-2-imine, 1,7,7-Trimethyl-*N*-nitro-3-nitrosobicyclo[2.2.1]hept-2-en-2-amine and their Reactions with Nitrogen Nucleophiles.

Angelo Ranise, Francesco Bondavalli, and Pietro Schenone*
Istituto di Scienze Farmaceutiche dell'Università, Viale Benedetto XV, 3-16132 Genova, Italy

The potassium salt (**2**) of 1,7,7-trimethyl-*N*-nitrobicyclo[2.2.1]heptan-2-imine (**1**) reacted with bromine in both acid and alkaline solutions to give, in high yields, 3-*exo*-bromo-1,7,7-trimethyl-*N*-nitrobicyclo[2.2.1]heptan-2-imine (**3**) and 3,3-dibromo-1,7,7-trimethyl-*N*-nitrobicyclo[2.2.1]heptan-2-imine (**8**), respectively. On reaction with morpholine, (**3**) underwent a bromine epimerization to afford, in high yield, 3-*endo*-bromo-1,7,7-trimethyl-*N*-nitrobicyclo[2.2.1]heptan-2-imine (**5**), whereas 3-*endo*-bromo-1,7,7-trimethylbicyclo[2.2.1]heptan-2-imine (**4**) was obtained from (**3**) with ammonia. Nitrimine (**5**) reacted with aniline to afford 3-*endo*-bromo-1,7,7-trimethyl-*N*-phenylbicyclo[2.2.1]-heptan-2-imine (**7**). Reaction of (**2**) with nitrous acid gave 1,7,7-trimethyl-*N*-nitro-3-nitrosobicyclo-[2.2.1]hept-2-en-2-amine (**9**) in high yield; this behaved in part as the tautomeric 3-hydroxyimino-1,7,7-trimethyl-*N*-nitrobicyclo[2.2.1]heptan-2-imine to afford with ammonia, hydrazine, and primary amines the corresponding *N*-substituted 3-hydroxyimino-1,7,7-trimethylbicyclo[2.2.1]heptan-2-imines in high yields.

Angeli and Rimini[1] reported the preparation of the so-called 'bromopernitrosocamphor' ($C_{10}H_{15}BrN_2O_2$) by reaction of 'pernitrosocamphor'[2] with bromine in acetic–hydrobromic acid solution, which on alkali treatment then gave the isomeric 'isobromopernitrosocamphor'. Although these results were later confirmed,[3] other authors[4] found that the above reaction gave a complex mixture containing small amounts of the two unidentified isomers. Clarification of the 'pernitrosocamphor' structure as that of 1,7,7-trimethyl-*N*-nitrobicyclo-[2.2.1]heptan-2-imine (**1**)[5] led to its being considered, *via* its resonance structures, as a form of camphor, the carbonyl group of which was activated towards nucleophilic attack.[6] In an alternative explanation for the reaction, the known stability of the potassium salt of (**1**) suggested that abstraction of a C-3 proton from (**1**) by a base would give the stable anion (**2**), the negative charge being delocalized over three centres, of which that on C-3 would possess particularly strong nucleophilic properties.

These considerations, and our interest in the nitrimino group chemistry,[6] prompted us to reconsider the Angeli and Rimini reaction as a particular case of electrophilic attack on the nucleophile (**2**), and to extend this reaction to other electrophiles, such as nitrous acid.

Results and Discussion

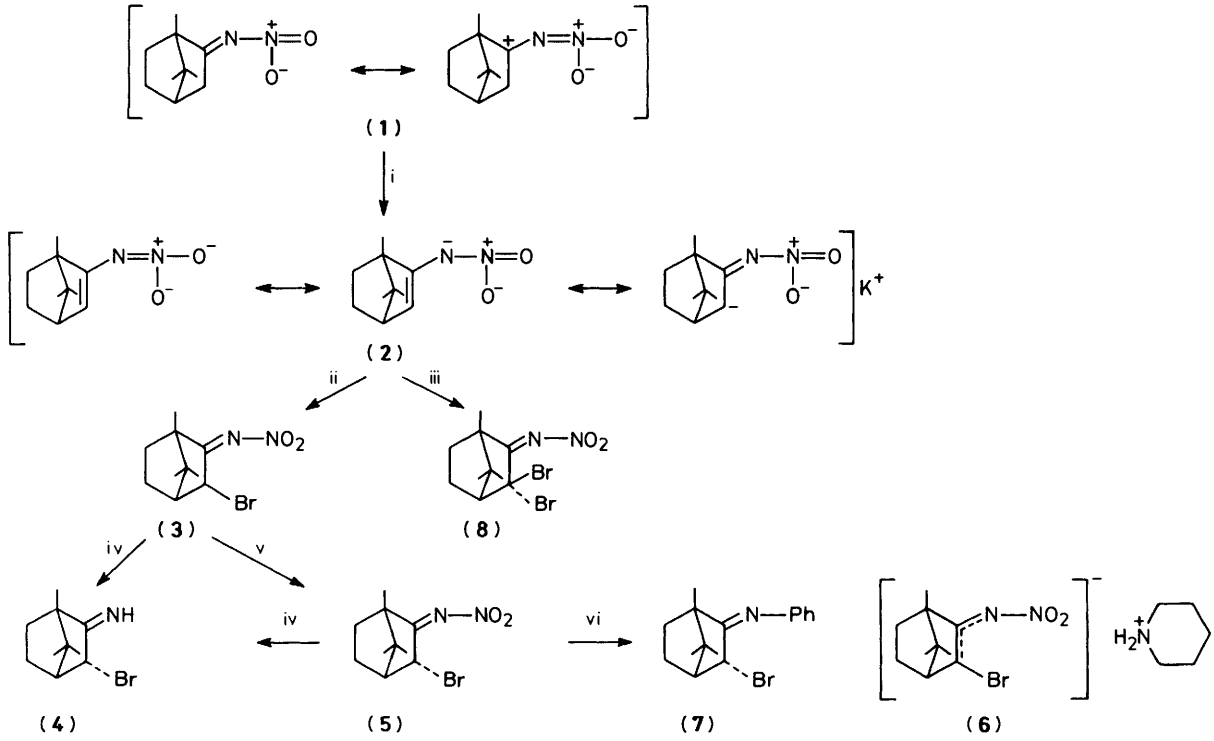
As a first consideration, it must be emphasized that success in the described reactions is closely connected with the experimental procedure. Thus, preliminary work showed that the salt (**2**) prepared *in situ* in ethanol must be added to the ethanol solution of the electrophilic reagent in order to avoid the recovery of the camphor nitrimine (**1**). Upon optimization of the experimental conditions, reactions could be carried out on a molar scale with yields of 90% or more.

The reaction of (**2**) with bromine was carried out both in strong acid (hydrogen chloride) and basic (potassium hydroxide) solutions (Scheme 1). In the former case a product, m.p. 114 °C, corresponding in this respect to 'bromopernitrosocamphor', was obtained in 60% yield. This compound is 3-*exo*-bromo-1,7,7-trimethyl-*N*-nitrobicyclo[2.2.1]heptan-2-imine (**3**), as was shown by the presence of i.r. absorptions corresponding to C=N and N–NO_2 groups, ^{13}C n.m.r. evidence of a C=N–NO_2 group at δ 186.00 and a ^1H n.m.r. singlet at δ 4.72, similar to the *endo* C-3 proton of 3-*exo*-bromocamphor.[8] The formation of (**3**) arises as a result of direct attack of bromine on the carbanion site of (**2**).

Treatment of (**3**) with nucleophiles such as ammonia and secondary aliphatic amines gave different results according to the reagent employed. The reaction with ammonia afforded, in 92% yield, 3-*endo*-bromo-1,7,7-trimethylbicyclo[2.2.1]heptan-2-imine (**4**), whose structure was assigned on the basis of the presence of an i.r. absorption for the C=N groups and a ^1H n.m.r. doublet at δ 4.83 (*J* 4 Hz), typical of the 3-*exo*-proton in the bornane system,[8,9] as well as a broad signal for the imine proton at δ 7.3—8.0. Treatment of (**3**) with morpholine gave, in 91% yield, the epimeric product, namely 3-*endo*-bromo-1,7,7-trimethyl-*N*-nitrobicyclo[2.2.1]heptan-2-imine (**5**), which showed the same m.p. (66 °C) of 'isobromopernitrosocamphor'.

The structure of (**5**) was assigned on the basis of i.r. signals for C=N and N–NO_2 groups, a ^1H n.m.r. doublet at δ 5.25 (*J* 4 Hz), typical of 3-*exo*-H, and a ^{13}C n.m.r. signal at δ 184.56, typical of a C=N–NO_2 grouping.

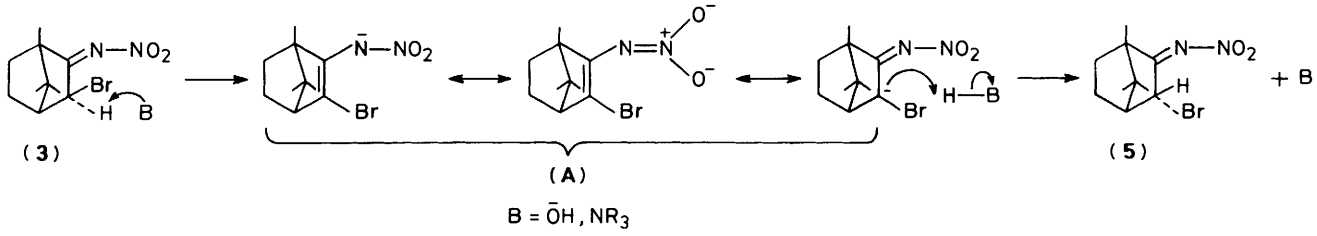
The use of morpholine as a secondary amine is critical in ensuring simple bromine epimerization since with piperidine, a stable salt (**6**) was formed; this decomposed on acid and alkaline treatment. In this reaction pyrrolidine gave an unstable liquid which could not be characterized. The salt (**6**) could also be obtained (91%) by treatment of (**5**) with piperidine in ether solution. Since the 3-bromo substituent makes the proton on the same carbon atom more acidic the basicity of the secondary amine is clearly important in ensuring activity. With aliphatic and aromatic primary amines, the epimerization of bromine was complicated by the condensation reaction with the nitrimino



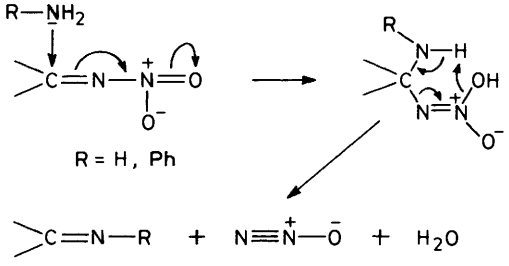
Scheme 1. *Reagents:* i, KOH; ii, Br_2–6M-HCl; iii, Br_2–KOH; iv, NH_3–EtOH; v, morpholine; vi, aniline

group (*vide infra*), giving rise to mixtures which were not investigated.

A tentative mechanism for the above reactions is shown in Schemes 2 and 3. The base (OH^-, NR_3) could cause epimerization of (**3**) to (**5**) by attack on 3-*endo*-H to form the stable anion (A), followed by reaction of the carbanion site of (A) with the conjugated acid to give the more stable *endo* C–Br bond. In this context, it should be noted that 3-*exo*-bromocamphor also epimerizes with alkali to give the 3-*endo* isomer.[10] The nitrimine (**5**) would then react with ammonia with loss of dinitrogen oxide and water to give (**4**) (Scheme 3), or may survive unchanged in the presence of more hindered secondary amines. The nitrimine (**5**) can indeed be an intermediate in the reaction of (**3**) with ammonia, since with this reagent it gave the imine (**4**) in nearly quantitative yield.



Scheme 2.



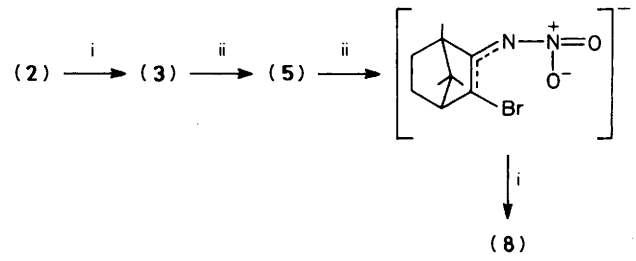
Scheme 3.

A transfer of oxygen from the nitro group to the nucleophile after the attack on C-2 appears in the mechanism of Scheme 3, a feature already suggested in the case of the reaction of (**1**) with cyanide ion.[11a] The nitrimine (**5**) showed a reactivity similar to that of camphornitrimine (**1**), *e.g.* it reacted with primary amines to give *N*-substituted imines with loss of dinitrogen oxide and water (Scheme 3, *cf.*[6]), but the reaction was satisfactory only with aniline to yield 3-*endo*-bromo-1,7,7-trimethyl-*N*-phenylbicyclo[2.2.1]heptan-2-imine (**7**).

Because of the mobility of the bromo substituent, amines such as benzylamine and cyclohexylamine gave condensation products which could not be obtained pure.

When bromination of (**2**) was carried out in potassium hydroxide solution, a third product m.p. 90—91 °C was obtained (91%), which we suggest is 3,3-dibromo-1,7,7-trimethyl-*N*-nitrobicyclo[2.2.1]heptan-2-imine (**8**) on the following grounds: mass spectral data confirm the presence of two bromine atoms; the i.r. spectrum showed the absorption of C=N and N–NO_2 groups; neither an olefin proton nor methine CHBr

were present in the ^1H n.m.r. spectrum, whereas the ^{13}C n.m.r. spectrum revealed the presence of a C=N nitrimino group at δ 182.86, *i.e.* a peak very similar to that shown by the nitrimines (**3**) and (**5**). The formation of (**8**) can be explained according to Scheme 4, whereby the first three steps are similar to those

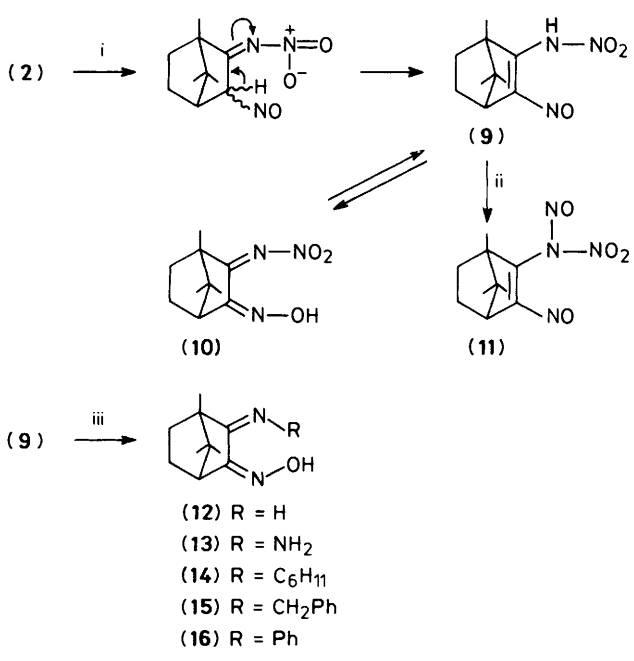


Scheme 4. *Reagents:* i, Br_2; ii, KOH

leading to nitrimine (**5**); a further step is due to the enhanced acidity of 3-H which gave a carbanion-iminate, whose further bromination on the carbon atom afforded the final product (**8**). The reaction of bromine both with (**3**) in the presence of 2 equiv. of KOH and with (**5**) in the presence of 1 equiv. of KOH gave (**8**) in nearly quantitative yield in all cases. Also salt (**6**) gave (**8**) in high yield by reaction with bromine.

The reaction of (**2**) with nitrous acid ($NaNO_2$ and concentrated HCl) afforded, in 94% yield, 1,7,7-trimethyl-*N*-nitro-3-nitrosobicyclo[2.2.1]hept-2-en-2-amine (**9**), whose structure was assigned from i.r. spectral data showing N–H stretching (3 550 cm^{-1}) and alkene and NO_2 absorptions; the ^1H n.m.r. spectrum confirmed the presence of a nitrogen proton.[11b]

Compound (**9**) could be nitrosated to yield 1,7,7-trimethyl-*N*-nitro-*N*,3-dinitrosobicyclo[2.2.1]hept-2-en-2-amine (**11**). Its reactions with ammonia and ammonia derivatives such as hydrazine and primary amines (Scheme 5) could be explained as



Scheme 5. *Reagents:* i, $NaNO_2$–11M-HCl; ii, $NaNO_2$–6M-HCl; iii, RNH_2

being due to the tautomer 3-hydroxyimino-1,7,7-trimethyl-*N*-nitrobicyclo[2.2.1]heptan-2-imine (**10**), *i.e.* a new nitrimine of the camphor series. Indeed (**9**) behaved with the above nitrogen nucleophiles like camphornitrimine (**1**) (see ref. 6), giving in high yields compounds (**12**)—(**16**) (*cf.* Scheme 3).

Two compounds corresponding to structure (**13**) are described in the literature,[12,13] but with different melting points. They are probably different geometric isomers; compounds (**12**) and (**13**) are strongly chelated, therefore 2-(*Z*) and 3-(*Z*) configurations are plausible.

In conclusion, the use of alkaline salts of nitrimino derivatives appears to be a new tool to enhance the reactivity of the parent compound towards electrophiles, and work is in progress to test the generality of the above reactions.

Experimental

M.p.s were determined with a Fisher-Johns apparatus. I.r. spectra were measured with a Perkin-Elmer 398 spectrophotometer. ^1H N.m.r. spectra were recorded on a Perkin-Elmer R-600 instrument (60 MHz) and ^{13}C n.m.r. spectra on a Varian FT-80 apparatus (80 MHz), using tetramethylsilane as internal standard. Mass spectra were obtained on a Varian Mat CH7A spectrometer. Ether refers to diethyl ether. Light petroleum refers to that fraction of b.p. 40—70 °C.

3-exo-*Bromo*-1,7,7-*trimethyl*-N-*nitrobicyclo*[2.2.1]*heptan*-2-*imine* (**3**).—Potassium hydroxide (29.74 g, 0.53 mol), dissolved in dry ethanol (100 ml), was added with vigorous stirring to a warm solution of camphornitrimine (**1**) (98.13 g, 0.5 mol) in dry ethanol (25 ml). The precipitated potassium salt (**2**) was dissolved by addition of water (75 ml) and the cold solution was added dropwise with stirring to a cooled (−5 °C) solution of bromine (26.2 ml, 0.51 mol) in 6M-HCl (90 ml) and ethanol (95%; 30 ml). Stirring was continued for 5 min, water (500 ml) was added, and the solution was extracted thoroughly with light petroleum–ether (1:3). The extracts were dried (Na_2SO_4), concentrated, and chromatographed on Florisil with ether as eluant to yield a mixture of 3-*exo*-bromo and 3-*endo*-bromo isomers (85:15 by ^1H n.m.r.), from which 3-exo-*bromocamphornitrimine* (**3**) was obtained as white needles (82.6 g, 60%), m.p. 114—115 °C, by recrystallization from light petroleum–ether (9:1) (Found: C, 44.0; H, 5.5; N, 10.4. $C_{10}H_{15}BrN_2O_2$ requires C, 43.7; H, 5.5; N, 10.2%); $\nu_{max.}$($CHCl_3$) 1 645 (C=N), 1 580 (NNO_2), and 1 310 cm^{-1} (NNO_2); δ_H($CDCl_3$) 1.02 (3 H, s. Me), 1.11 (3 H, s, Me), 1.27 (3 H, s, Me), 2.30 (1 H, br s, 4-H), and 4.72 (1 H, s, =CH); δ_C($CDCl_3$) 186.00, 56.00, 52.95, 48.43, 41.59, 30.68, 27.74, 22.01, 19.51, and 10.95; *m/z* 230 and 228 (M^+ − 46), 195, 149, 148, 134, 121, 109 (100%), and 107.

3-endo-*Bromo*-1,7,7-*trimethylbicyclo*[2.2.1]*heptan*-2-*imine* (**4**).—An ice-cooled, saturated solution of gaseous ammonia in dry ethanol (70 ml) was added to an ice-cooled solution of (**3**) (3.03 g, 11 mmol) in dry ethanol (30 ml), and the resulting solution was kept for 24 h in a refrigerator and for 12 h at room temperature. The solvent was removed under reduced pressure and the liquid residue gave, by bulb-to-bulb distillation under reduced pressure, 3-endo-*bromocamphorimine* (**4**) as a colourless liquid (2.33 g, 92%) which readily absorbed CO_2 from the air, b.p. 78—80 °C/0.2 mmHg (Found: C, 51.9; H, 7.1; N, 6.1. $C_{10}H_{16}BrN$ requires C, 52.2; H, 7.0; N, 6.1%); $\nu_{max.}$($CHCl_3$) 3 300 (NH) and 1 672 cm^{-1} (C=N); δ_H($CDCl_3$) 0.90 (3 H, s, Me), 1.07 (6 H, s, 2 Me), 2.10 (1 H, m, 4-H), 4.83 (1 H, d, *J* 4 Hz, 3-H), and 7.3—8.0 (1 H, br s, NH; disappears with D_2O); *m/z* 231 and 229 (M^+), 150, 123 (100%), 95, and 83.

3-endo-*Bromo*-1,7,7-*trimethyl*-N-*nitrobicyclo*[2.2.1]*heptan*-2-*imine* (**5**).—Morpholine (7 g, 0.08 mol) was added to a solution of (**3**) (35 g, 0.1272 mol) in dry toluene (150 ml) and the resulting solution was stirred for 2 h at room temperature and for 10 min at 70—80 °C. After cooling, the solution was washed with water

and 1M-HCl solution and then extracted with ether–light petroleum (1:1). The dried (Na_2SO_4) extracts were evaporated under reduced pressure and the residue was chromatographed on Florisil with ether as eluant to yield 3-endo-*bromocamphornitrimine* (**5**) as white crystals (32 g, 91%), m.p. 65—66 °C (80% EtOH) (Found: C, 43.7; H, 5.5; N, 10.1. $C_{10}H_{15}BrN_2O_2$ requires C, 43.7; H, 5.5; N, 10.2%); $\nu_{max.}$($CHCl_3$) 1 645 (C=N), 1 575 (NNO_2), and 1 310 cm^{-1} (NNO_2); δ_H($CDCl_3$) 0.98 (3 H, s, Me), 1.08 (3 H, s, Me), 1.12 (3 H, s, Me), and 5.25 (1 H, d, *J* 4 Hz, *exo*-3-H); δ_C($CDCl_3$) 184.56, 54.43, 50.47, 47.79, 45.35, 31.24, 22.96, 19.77, 19.11, and 10.80; *m/z* 230 and 228 ($M^+ - 46$), 195, 149, 148, 134, 121, 109 (100%), and 107.

Reaction of the Imine (**5**) *with Ammonia.*—Compound (**5**) (3.03 g, 11 mmol) was dissolved in a saturated solution of gaseous ammonia in dry ethanol (90 ml), which was warmed in a closed vessel at 80 °C for 2 h. After cooling, the solution was worked up as in the case of the reaction of (**3**) with ammonia to afford a liquid (2.3 g, 92%) showing the same b.p. and i.r. and n.m.r. spectral data as compound (**4**).

Preparation of Salt (**6**) *from the Imine* (**3**) *and Piperidine.*—Piperidine (1.5 ml, 15 mmol) was added at room temperature to a solution of (**3**) (3.03 g, 11 mmol) in anhydrous ether (20 ml). The mixture was stirred for a short time and allowed to stand for 1 h. A light-yellow solid separated which was filtered off, washed with light petroleum, and dried (3.70 g, 93%), m.p. 105—120 °C (decomp.) [from methanol–ether (1:2)] (Found: C, 49.8; H, 7.4; N, 11.6. $C_{15}H_{26}BrN_3O_2$ requires C, 50.0; H, 7.3; N, 11.7%); $\nu_{max.}$(KBr) 3 000—2 700 ($\overset{+}{N}H_2$) and 1 615 cm^{-1} (conjugated C=C); δ_H($CDCl_3$) 0.98 (3 H, s, Me), 1.08 (3 H, s, Me), 1.12 (3 H, s, Me), 3.42 (1.5 H, s, 1/2 3-H and NH; 1 H disappeared with D_2O), and 5.25 (0.5 H, d, *J* 5 Hz, 1/2 3-H); *m/z* 231 and 229 ($M^+ - 46 - 84$), 203, 201, 148, 122, 109, and 84 (100%).

Preparation of Salt (**6**) *from the Imine* (**5**) *and Piperidine.*—Following the above described procedure, compound (**5**) (3.03 g, 11 mmol) gave 3.61 g (91%) of salt (**6**).

3-endo-*Bromo*-1,7,7-*trimethyl*-N-*phenylbicyclo*[2.2.1]*heptan*-2-*imine* (**7**).—A mixture of (**5**) (11.0 g, 0.04 mol) and aniline (11.0 g, 0.118 mol) was warmed for exactly 10 min on a boiling water-bath. After cooling, water (50 ml) and then 1M-HCl solution were added until pH *ca.* 0 was reached. The mixture was extracted with ether and the extracts were dried (Na_2SO_4) and evaporated. The residue was chromatographed on Florisil using ether as eluant to afford 3-endo-*bromo*-N-*phenylcamphorimine* (**7**) as a red, viscous oil (10.1 g, 82%), b.p. 145—150 °C/0.1 mmHg (waxy solid) (Found: C, 63.1; H, 6.7; N, 4.9. $C_{16}H_{20}BrN$ requires C, 62.8; H, 6.6; N, 4.6%); $\nu_{max.}$($CHCl_3$) 1 680 cm^{-1} (C=N); δ_H($CDCl_3$) 0.98 (3 H, s, Me), 1.08 (6 H, s, 2 Me), 5.00 (1 H, d, *J* 5 Hz, *exo*-3-H), and 6.6—6.9 and 7.0—7.5 (5 H, 2 m, Ph); *m/z* 307 and 305 (M^+), 230, 228, 226, 149, 148, 123, 109 (100%), 95, and 83.

3,3-*Dibromo*-1,7,7-*trimethyl*-N-*nitrobicyclo*[2.2.1]*heptan*-2-*imine* (**8**).—To an alkaline solution of the salt (**2**) [prepared as in the case of (**3**) from (**1**) (6 g, 30.6 mmol) and potassium hydroxide (4.85 g, 86.4 mmol) in dry ethanol (50 ml), followed by dissolution with water (20 ml)], bromine (*ca.* 6 ml) was added dropwise at room temperature until a faint orange colour persisted. The mixture was stirred for 10 min, water (150 ml) was added, and excess of bromine was destroyed with sodium thiosulphate. The solution was extracted with ether–light petroleum (3:1), and the extracts were concentrated and chromatographed on Florisil with ether as eluant to yield 3,3-*dibromocamphornitrimine* (**8**) as a viscous oil (9.9 g, 91.5%) which solidified, m.p. 90—91 °C [from light petroleum–ether (7:1)] (Found: C, 34.0; H, 3.9; N, 7.9. $C_{10}H_{14}Br_2N_2O_2$ requires C, 33.9; H, 4.0; N, 7.9%); $\nu_{max.}$($CHCl_3$) 1 650 (C=N), 1 580 (NNO_2), and 1 320 cm^{-1} (NNO_2); δ_H($CDCl_3$) 1.10 (3 H, s, Me), 1.14 (3 H, s, Me), 1.35 (3 H, s, Me), and 2.80 (1 H, br s, 4-H); δ_C($CDCl_3$) 182.86, 60.14, 58.63, 49.20, 30.10, 28.93, 24.42, 22.13, and 9.84; *m/z* 310, 308 and 306 ($M^+ - 46$), 256, 254, 231, 229, 195, 149, 148, 134, 121, and 109 (100%).

Reaction of the Imine (**3**) *with Bromine.*—A solution of potassium hydroxide (1.23 g, 22 mmol) in dry ethanol (40 ml) was added to the imine (**3**) (3.03 g, 11 mmol) dissolved in the same solvent (15 ml). To the solution obtained after adding water (10 ml), bromine (*ca.* 1.5 ml) was added dropwise at room temperature until a faint orange colour persisted. Water (200 ml) was added and excess of bromine was destroyed with sodium thiosulphate. The solution was extracted with ether–light petroleum (1:1), and the extracts were dried ($MgSO_4$) and evaporated to give a viscous oil which solidified (3.70 g, 95%); its m.p. and i.r. and n.m.r. spectral data were identical with those of compound (**8**).

Reaction of the Imine (**5**) *with Bromine.*—This reaction was carried out just as above starting from the imine (**5**) (3.03 g, 11 mmol), but in the presence of potassium hydroxide (0.62 g, 11 mmol); yield of compound (**8**), 3.75 g (96%).

Reaction of the Salt (**6**) *with Bromine.*—Bromine (*ca.* 1.3 ml) was added dropwise at room temperature to a solution of the salt (**6**) (2.52 g, 7 mmol) in 95% ethanol (60 ml) and water (20 ml), until a faint orange colour persisted. The solution was then worked up as for the reaction of the imine (**3**) with bromine; yield of compound (**8**), 2.16 g, (87%).

1,7,7-*Trimethyl*-N-*nitro*-3-*nitrosobicyclo*[2.2.1]*hept*-2-*en*-2-*amine* (**9**).—Sodium nitrite (60 g) dissolved in water (100 ml) was added to a solution of the salt (**2**), prepared as in the case of the imine (**3**) from (**1**) (60 g, 0.306 mol) and potassium hydroxide (18.2 g, 0.324 mol) in dry ethanol (75 ml), plus 95% ethanol (50 ml) to complete the dissolution. The solution was added as a single portion to an ice-cooled solution of 11M-HCl (220 ml) to which sodium nitrite (60 g) had just been added (**CAUTION**: use a good ventilated hood). After the evolution of nitrogen oxides subsided, water (800 ml) was added and the solution was extracted thoroughly with ether. The combined extracts were dried (Na_2SO_4) and evaporated to give N-*nitro*-3-*nitrosocamphorenamine* (**9**) as a white solid (65 g, 94%). An analytical sample was obtained by chromatography on Florisil with ether as eluant, m.p. 152—153 °C [from light petroleum–ether (9:1)] (lit.,[11b] 147·5 °C) (Found: C, 53.2; H, 6.6; N, 18.6. $C_{10}H_{15}N_3O_3$ requires C, 53.3; H, 6.7; N, 18.65%); $\nu_{max.}$($CHCl_3$) 3 550 (NH), 1 640 (C=C), 1 570 (NNO_2,NO), and 1 310 cm^{-1} (NNO_2); δ_H($CDCl_3$) 0.98 (3 H, s, Me), 1.04 (3 H, s, Me), 1.15 (3 H, s, Me), 3.26 (1 H, br s, 4-H), and 8.55 (1 H, br s, NH; disappears with D_2O); *m/z* 179 ($M^+ - 46$, 100%), 163, 161, 134, 121, 109, and 95.

1,7,7-*Trimethyl*-N-*nitro*-N,3-*dinitrosobicyclo*[2.2.1]*hept*-2-*en*-2-*amine* (**11**).—A solution of the amine (**9**) (3 g, 13.4 mmol) in ether (10 ml) was added to 6M-HCl (50 ml), followed by dropwise addition of sodium nitrite (9 g, 0.13 mol) dissolved in water (10 ml). The solution was stirred at room temperature for 15 h under a slight pressure (mercury valve) and extracted thoroughly with ether. The dried (Na_2SO_4) extracts were concentrated and chromatographed on Florisil with ether as eluant to yield N-*nitro*-N,3-*dinitrosocamphorenamine* (**11**) as white crystals (2.5 g, 73%), m.p. 115—116 °C [from light petroleum–ether (1:11)] (Found: C, 47.4; H, 5.6; N, 22.1. $C_{10}H_{14}N_4O_4$ requires C, 47.2; H, 5.5; N, 22.0%); $\nu_{max.}$(KBr) 1 635 (C=C), 1 590, 1 580 (NNO_2,NO), and 1 310 cm^{-1} (NNO_2);

$\delta_H(CDCl_3)$ 1.06 (3 H, s, Me), 1.08 (3 H, s, Me), 1.20 (3 H, s, Me), and 2.90 (1 H, br s, 4-H); *m/z* 208 ($M^+ - 46$), 162, 161, 147, 135, 109, 105, 95, and 46 (100%).

3-*Hydroxyimino*-1,7,7-*trimethylbicyclo*[2.2.1]*heptan*-2-*imine* (**12**).—Compound (**9**) (2.50 g, 0.011 mol) was dissolved into a saturated solution of gaseous ammonia in dry ethanol (50 ml) cooled at −5 °C, and the resulting solution was stored in a refrigerator for 24 h with occasional stirring. By distillation of ethanol under reduced pressure, 3-*hydroxyiminocamphorimine* (**12**) was obtained as a white solid (1.95 g, 98%), m.p. 186—187 °C (CH_2Cl_2) (Found: C, 66.5; H, 8.9; N, 15.6. $C_{10}H_{16}N_2O$ requires C, 66.6; H, 8.95; N, 15.5%); $\nu_{max.}(CHCl_3)$ 3 570 (OH), 3 250—2 500 (chelated NH), 1 695 (C=C), and 1 635 cm^{-1} (C=N); $\delta_H[(CD_3)_2SO]$ 0.72 (3 H, s, Me), 0.93 (3 H, s, Me), 0.99 (3 H, s, Me), 2.98 (1 H, d, *J* 3.5 Hz, 4-H), 9.5—9.9 (1 H, m, NH; disappears with D_2O), and 11.33 (1 H, br s, OH; disappears with D_2O); *m/z* 180 (M^+), 163, 152, 136 (100%), 121, 109, and 95.

3-*Hydroxyimino*-1,7,7-*trimethylbicyclo*[2.2.1]*heptan*-2-*one Hydrazone* (**13**).—Anhydrous hydrazine (0.8 ml, 25 mmol) was added as a single portion to a stirred, ice-cooled solution of the amine (**9**) (2.50 g, 11 mmol) in dry ethanol (20 ml). Stirring was continued for 10 min after which the solvent and excess of hydrazine were removed under reduced pressure; the residue was washed with light petroleum to give t.l.c. pure 3-*hydroxyiminocamphor hydrazone* (**13**) as a white solid (1.95 g, 91%), m.p. 193—195 °C from MeOH–CH_2Cl_2 (1:1) (lit.[12,13] m.p. 142, 125—126 °C) (Found: C, 61.4; H, 8.8; N, 21.3. $C_{10}H_{17}N_3O$ requires C, 61.5; H, 8.8; N, 21.5%); $\nu_{max.}$(KBr) 3 415, 3 320 (NH_2), 3 300—2 600 (chelated OH), 1 625 (C=N), and 1 605 cm^{-1} (C=N); $\delta_H[(CD_3)_2SO]$ 0.80 (6 H, s, 2 Me), 1.34 (3 H, s, Me), 2.95 (1 H, d, *J* 3.5 Hz, 4-H), 6.12 (2 H, br s, NH_2; disappears with D_2O), and 10.30 (1 H, s, OH; disappears with D_2O); *m/z* 195 (M^+), 178, 166, 162, 148, 134 (100%), 120, 108, 94, and 83.

General Procedure for the Preparation of N-*Substituted* N-*Hydroxyimino*-1,7,7-*trimethylbicyclo*[2.2.1]*heptan*-2-*imines* (**14**)—(**16**).—The primary amine (10.5 mmol) was added to the amine (**9**) (2.30 g, 10.2 mmol) dissolved in dry toluene (30 ml), and the resulting solution was stirred for 10 min on a boiling steam-bath. The solvent was removed under reduced pressure and the residue was chromatographed on Florisil with ether as eluant, yielding white solids which were recrystallized from a suitable solvent to give the following products. N-*Cyclohexyl*-3-*hydroxyimino*-1,7,7-*trimethylbicyclo*[2.2.1]*heptan*-2-*imine* (**14**) (95%), m.p. 182—183 °C (ether) (Found: C, 73.3; H, 10.1; N, 10.6. $C_{16}H_{26}N_2O$ requires C, 73.2; H, 10.0; N, 10.7%); $\nu_{max.}(CHCl_3)$ 3 570 (OH), 3 300—3 100 (chelated OH), 1 675 (C=N), and 1 620 cm^{-1} (C=N); $\delta_H[(CD_3)_2SO]$ 0.70 (3 H, s, Me), 0.90 (6 H, s, 2 Me), 3.12 (1 H, d, *J* 3.5 Hz, 4-H), and 11.20 (1 H, br s, OH; disappears with D_2O); *m/z* 262 (M^+), 245 (100%), 205, 176, 164, 136, and 109.

N-*Benzyl*-3-*hydroxyimino*-1,7,7-*trimethylbicyclo*[2.2.1]*heptan*-2-*imine* (**15**) (95%), m.p. 115—117 °C [from light petroleum–ether (9:1)] (Found: C, 75.8; H, 8.3; N, 10.4. $C_{17}H_{22}N_2O$ requires C, 75.5; H, 8.2; N, 10.4%); $\nu_{max.}(CHCl_3)$ 3 570 (OH), 3 300—3 100 (chelated OH), 1 680 (C=N), and 1 625 cm^{-1} (C=N); $\delta_H(CDCl_3)$ 0.78 (3 H, s, Me), 0.90 (3 H, s, Me), 1.08 (3 H, s, Me), 3.20 (1 H, br s, 4-H), 5.08 (2 H, d, *J* 4.5 Hz, CH_2Ph), 7.26 (5 H, s, Ph), and 10.30 (1 H, br s, OH; disappears with D_2O); *m/z* 270 (M^+), 253 (100%), 242, 165, 149, 137, 109, and 91.

3-*Hydroxyimino*-1,7,7-*trimethyl*-N-*phenylbicyclo*[2.2.1]*heptan*-2-*imine* (**16**) (83%), m.p. 184—185 °C [from light petroleum–ether (1:1)] (Found: C, 75.2; H, 7.9; N, 10.9. $C_{16}H_{20}N_2O$ requires C, 75.0; H, 7.9; N, 10.9%); $\nu_{max.}(CHCl_3)$ 3 560 (OH), 3 400—3 100 (chelated OH), 1 690 (C=N), and 1 635 cm^{-1} (C=N); $\delta_H(CDCl_3)$ 0.94 (3 H, s, Me), 0.97 (3 H, s, Me), 1.10 (3 H, s, Me), 3.13 (1 H, br s, 4-H), 6.5—6.9 and 7.0—7.6 (5 H, 2 m, Ph), and 8.12 (1 H, br s, OH; disappears with D_2O); *m/z* 256 (M^+), 239, 197, 144, 136, 109, and 104 (100%).

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