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α,β-UNSATURATED NITROSO SYSTEM—I

THE GENERATION AND TRANSFORMATIONS OF ω-NITROSO CAMPHENE†

S. RANGANATHAN,* B. B. SINGH and C. S. PANDA
Department of Chemistry, Indian Institute of Technology, Kanpur 208016, U.P., India

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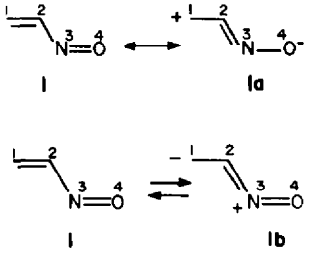
Abstract—MO calculations predict a pronounced 1,4-dipolar character for the α,β-unsaturated nitroso synthon, much above that for traditional systems like the α,β-unsaturated Nitro and α,β-unsaturated carbonyl. The work on ω-nitroso camphene-generated from *inter alia* ω-Nitrocamphene **3** is in agreement with the expectations. Thus, the **3** → tricyclene aldehyde **4** change is rationalized on the basis of a σ shift and the **5** → **20** and **6** → **21** changes highlight the overwhelming influence of the α,β-unsaturated nitroso synthon over even the enol ether and enamine functions present in **5** and **6**. Amongst other noteworthy features are the deep seated **3** → **8** rearrangement and the preparation and transformation of the extraordinarily stable and the first reported bridgehead nitrile oxide **14**.

Astonishingly, the α,β-unsaturated nitroso system **1** has thus far escaped characterization.[1] The elusiveness of this grouping is revealed from HMO calculations which reflect the pronounced 1,4-dipolar contribution **1a** over the possible 1,3-dipolar contribution **1b** as evidenced by the 2,3-πbond order and charge densities:

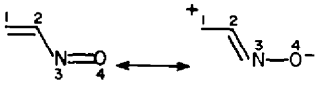
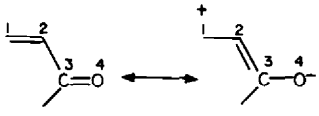
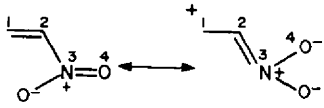
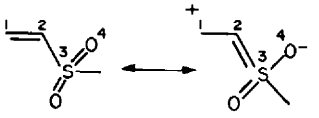
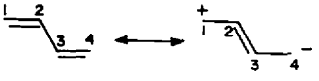


Bonds	π-Bond order		Charge density
1–2	0.399	1	0.263
2–3	0.783	2	0.624
		3	1.270
3–4	0.331	4	1.843

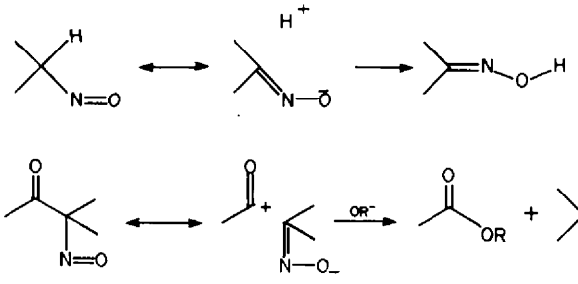
Additionally, these calculations show that the α,β-unsaturated nitroso system is by far the most effective "Michael acceptor" as demonstrated by a 1,4-dipolar contribution very significantly above that of the traditional Michael acceptors such as the α,β-unsaturated carbonyl system and the α,β-unsaturated nitro system (Table 1).

The nitroso group, in turn, receives significant contribution from the polar form which is in excellent agreement with the well known transformation of secondary nitroso compounds to the corresponding oximes and the ready carbon–carbon bond cleavage of tertiary nitroso compounds:[2]

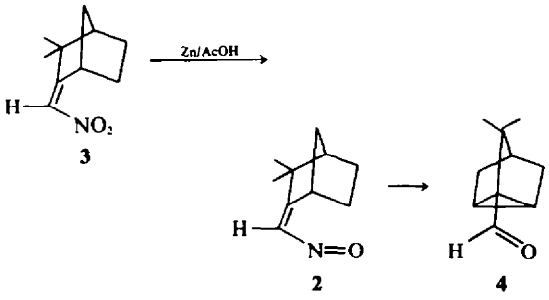
Table 1.

Michael acceptor	1–2	2–3	3–4
	0.399	0.783	0.331
	0.846	0.518	0.583
	0.807	0.460	0.546
	0.938	0.339	0.622
	0.894	0.447	0.894

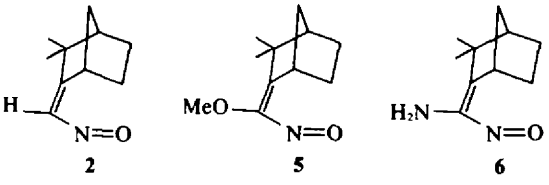
†Respectfully dedicated to Prof. ROBERT BURNS WOODWARD on the occasion of his sixtieth birthday.



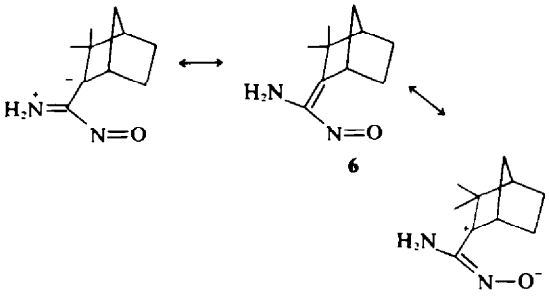
On the basis of these, the α,β-unsaturated nitroso grouping would be a powerful electrophile. Amongst the few reactions described in the literature that could possibly take place via α,β-unsaturated nitroso grouping,[1,3] the most promising case for detailed examination appeared to be ω-nitroso camphene **2**. The appealing features of this system are that it is sterically encumbered—thus moderating the high reactivity—and has possibilities for *sigma* participation and rearrangement. Indeed the genesis for our interest in α,β-unsaturated nitroso systems stems from the transformation of ω-nitro camphene **3** to tricyclene aldehyde **4**:



In the present work ω-nitroso camphene has been generated by different procedures. The behaviour of ω-nitroso camphenes **2**, **5** and **6** are in good agreement with the pronounced reactivity anticipated from the α,β-unsaturated nitroso grouping:

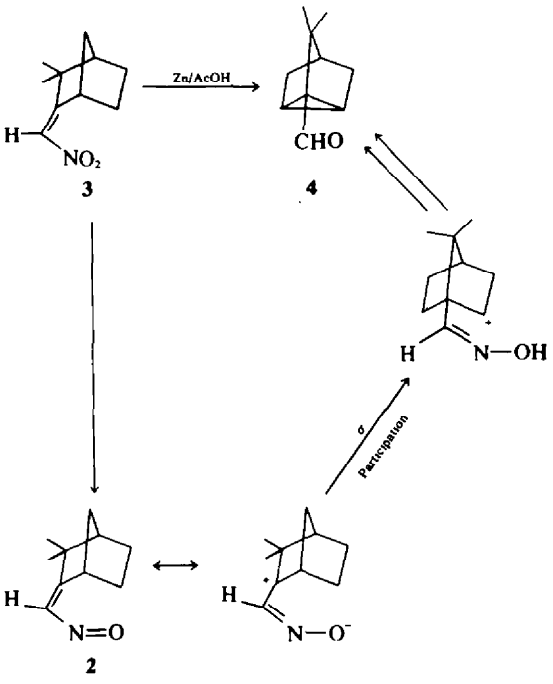


All these spontaneously accept nucleophiles in contrast to the α,β-unsaturated nitro system, ω-nitrocamphene **3**. ω-Amino-ω-nitroso camphene **6** can be considered as an enamine as well as an α,β-unsaturated nitroso system. The enamine contribution would make the β-carbon electron rich in contrast to the α,β-unsaturated dipole which would make this centre electron poor:

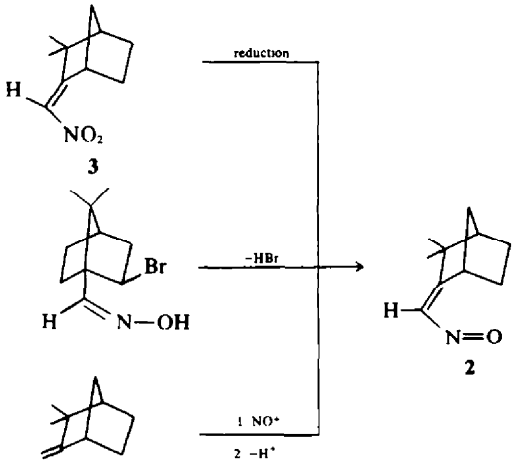


The spontaneous acceptance of nucleophiles by **6** (*vide infra*) clearly demonstrates the highly electrophilic character generated by the α,β-unsaturated nitroso system.

In 1940, Lipp, Braucker and Sauer[4] reported the unusual transformation of ω-nitrocamphene **3** to tricyclene aldehyde **4** with zinc and acetic acid. We rationalized the fascinating **3**→**4** change on the basis of involvement of ω-nitroso camphene **2** as an intermediate:

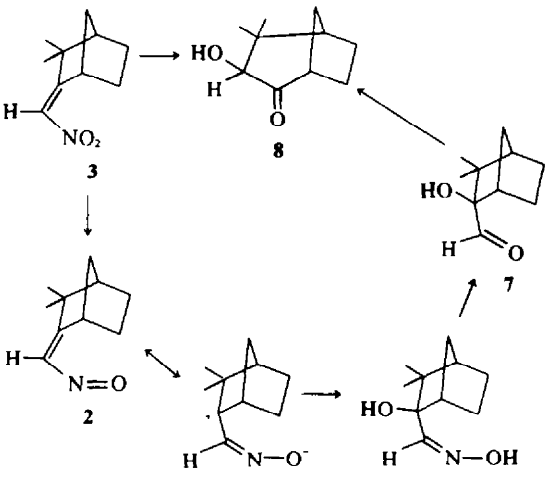


Lipp's own explanation for the **3**→**4** change on the basis of initial acceptance of elements of acetic acid by **3** was immediately discounted on the finding that **3** is inert to acetic acid treatment under conditions of the **3**→**4** change. In our hands, the **3**→**4** change was found to give rise to a complex mixture from which pure tricyclene aldehyde could be isolated in low yields. It was, therefore, considered of interest to explore rational routes to **2** by the following procedures:

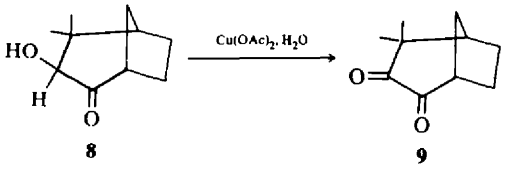


"ω-Nitroso camphene" by reduction of ω-nitrocamphene. Chromium(II) species has been recognized as a reagent that could reduce the nitro function in discrete steps.[5] Reaction of **3** with freshly prepared chromous chloride gave, in 78% yield, the acyloin **8**. This remarkable change can be readily understood in terms of acceptance of elements of water by the initially formed ω-nitroso camphene followed by oxime hydrolysis and the

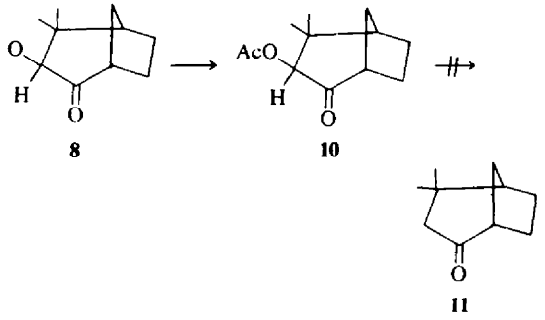
well documented α-hydroxy aldehyde to acyloin transformation.[6]



The structural assignment of **8** is supported by analysis, IR and NMR† and also by chemical studies. The alternative structure involving the transposition of the C=O and OH group was ruled out on the basis of the appearance of the non-bridgehead tertiary proton as a sharp singlet. The acyloin was oxidized with cupric acetate[7] in excellent yields to the corresponding diketone **9**.†[8]



Efforts to transform **8** to corresponding carbonyl compound **11** by reduction of the acetyl derivative **10**† with zinc-acetic acid or zinc-acetic anhydride were unsuccessful:[9]

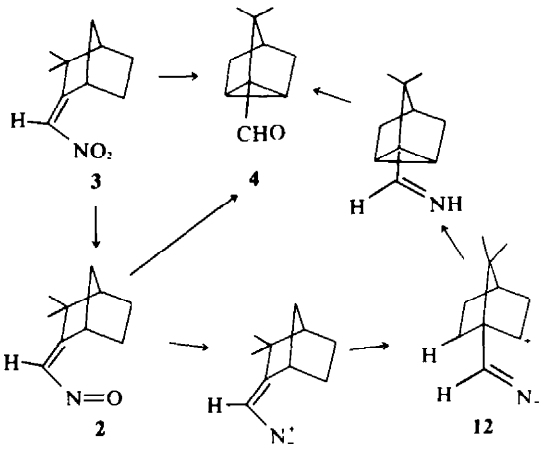


The acetate has been fully characterized by analysis, IR and NMR.† Our failure to effect reduction of this compound can be readily rationalized on the basis of an equatorial disposition of the acetoxyl function in **10** wherein the necessary condition for elimination, namely a coplanar relationship between the carbonyl and C–OAc bond, are not satisfied.[10] The hydroxyl group in **8**, should therefore be equatorial.

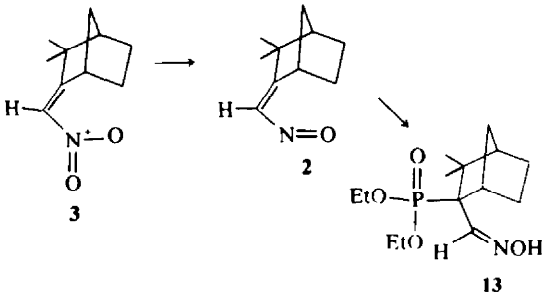
†Routine spectral and analytical data are presented in the Experimental.

The transformation of α-hydroxyl aldehydes to acyloins is a well known reaction and has been extensively studied in the case of steroids.[11] The **3**→**8** change represents the most facile entry into substituted bicyclo(3,2,1)octanes.

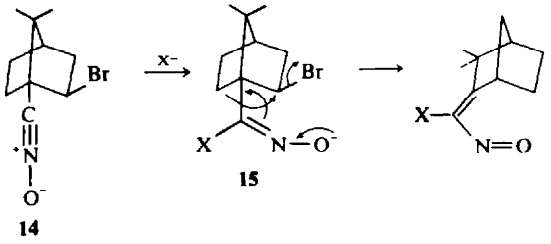
The reaction of **3** with triethyl phosphite, was studied in the hope that this would lead to the production of the α,β-unsaturated nitroso compound **2** which in turn could undergo fast deoxygenation and then to the tricyclene aldehyde **4** by the following pathways:



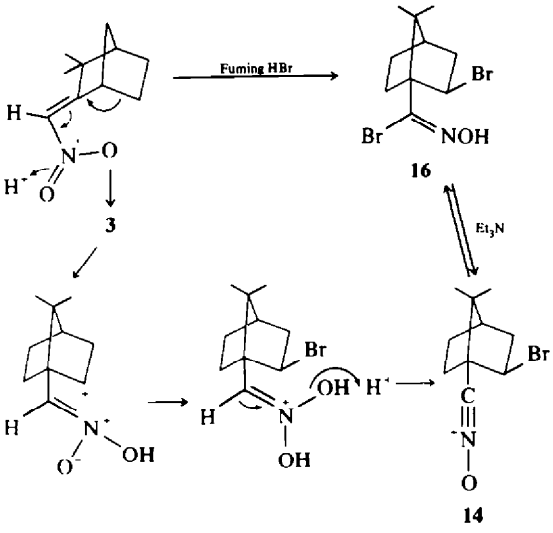
A solution of **3** in triethyl phosphite on refluxing under nitrogen for 14 h showed no starting material and work up involving quick chromatography and distillation gave a pale yellow oil to which structure **13** has been tentatively assigned on the basis of analysis, IR and NMR. The **3**→**13** change could be rationalized on the basis of the addition of triethyl phosphite to **2** generated *in situ*:



ω-Nitroso comphene via transformation of an unusual bridgehead nitrile oxide. Yet another strategy to ω-nitroso camphene involved the combination of the currently well recognized nucleophilic participation from bridged position[12] with the possible formation of α,β-unsaturated nitroso systems from β-halooximes. It was envisaged that these two processes would take place with great ease in the intermediate **15** formed from the nitrile oxide precursor **14**:

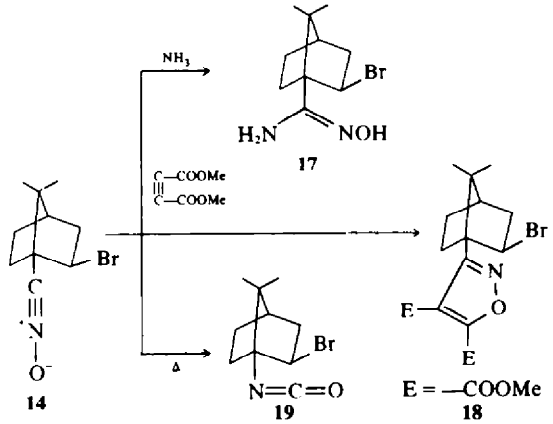


Bridgehead nitrile oxide **14** was prepared in quantitative yields by the action of triethylamine or ammonia on the *exo* - 2 - bromo - 7,7 - dimethylbicyclo(2,2,1)heptane - 1 - bromoaldoxime **16**.†[13] Compound **16** was in turn prepared essentially as described by Lipp[14] by treatment of ω-nitrocamphene **3** with fuming hydrobromic acid. Interestingly the **3**→**16** change should involve the nitrile oxide **14** as an intermediate. The formation of **16** from **14** could be readily rationalized on the basis of addition of elements of hydrobromic acid:



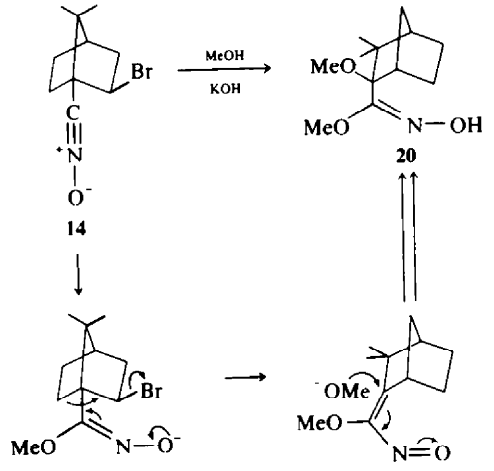
To our knowledge, the nitrile oxide **14** is the first bridgehead nitrile oxide described.

The most interesting property of **14** is its unusual stability, since as a rule, nitrile oxides are highly prone to dimerization or addition. The nitrile oxide **14** could be crystallized from boiling hexane, is unchanged on melting or absolute alcohol at room temperature and excess ammonia for few minutes; however, the nitrile oxide behaves in an expected manner to form adducts with ammonia and dimethyl acetylene dicarboxylate on overnight treatment in ether giving rise to compounds **17**† and **18**. Further, as is the case with stable nitrile oxides, **14** undergoes smooth transformation to the bridgehead isocyanate **19**:†

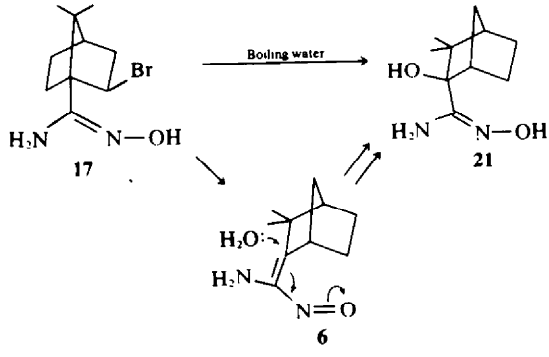


Interestingly the nitrile oxide **14** has opened up a useful method for the preparation of 2-bromo-1-heterocycles as exemplified by **18**.

The expected bridged participation and halide elimination took place on treatment of the nitrile oxide **14** with methanolic KOH at room temperature leading to the clean formation of the methoxy amidoxime **20**.† This reaction should be considered remarkable since it demonstrates the capability of substituted bridgehead oximes to effect intramolecular displacement reactions under mild conditions and in strongly alkaline media.



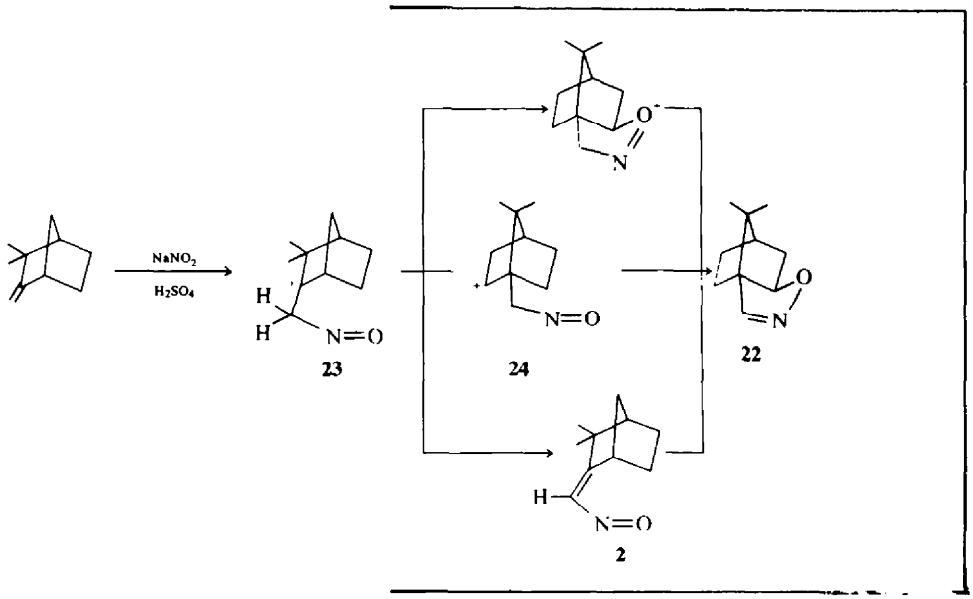
The stereochemical assignment in **20** is based on the preferred *exo* attack of the methoxide ion. The amidoxime **17** which can be obtained readily by the addition of the elements of ammonia to nitrile oxide **14** undergoes the rather uncommon bornane→camphenilane change via nucleophilic displacement from a bridgehead position. Indeed, boiling of **17** in water or treatment at room temperature with $AgNO_3$ gives the hydroxy amidoxime **21**† via the ω-nitroso camphene **6**:



In all these cases, particularly in the case of amidoxime **17**, no **1–6** sigma bond participation leading to the tricyclene aldehyde was observed. In these cases, the α,β-unsaturated nitroso system intimately associated with the polar solvent envelope, undergoes ready collapse in preference to sigma participation.

ω-Nitroso camphene via electrophilic substitution of camphene. The camphene→**22** transformation provides a facile route to doubly functionalized bornanes. The structural assignment for **22** is supported by analysis, IR, NMR and UV.† This change can be rationalized on the basis of further transformation of electron deficient species **23**, via 1,6-σ-participation, O–C bond formation and proton loss. It has been found that optically active camphene gives optically active **22**, thus indicating that

the O–C bond formation must be synchronous with σ-participation. If σ-participation were to precede O–C bond formation, the resulting intermediate bornane cation **24** would certainly racemize via very rapid hydride shifts.[15] The question as to whether deprotonation succeeds or precedes the concerted change cannot be answered. If the latter were to be the case, the isoxazoline formation would be, formally, a $\pi 4s + \sigma 2s$ change involving the novel α,β-unsaturated nitroso system **2**, which has been demonstrated to behave as powerful 1,4-dipoles:[16]



EXPERIMENTAL

M.ps were taken on a Fisher–John m.p. apparatus and are uncorrected. Capillary m.ps were taken in a Thomas Hoover capillary m.p. apparatus. IR spectra were recorded either on a Perkin Elmer 137 or Perkin Elmer 521 Spectrophotometer. NMR spectra were determined either with chloroform-d_1 or CCl_4 or trifluoro acetic acid solutions on a Varian A-60 or A60D Spectrometer at 60 mHz using TMS as internal standard. Silica gel G (Stahl) with calcium sulphate binder was used for TLC. Column chromatography was performed either with silica gel or with alumina. The compounds reported here, unless otherwise stated, are optically inactive.

ω-Nitro camphene **3**. To an ice cooled and stirred mixture of petroleum ether (b.p. 40–60°) soln of camphene (81.6 g, 0.6 mole, 200 ml) and aq. $NaNO_2$ (660 g, 9.5 mole, 400 ml) was added in drops over a period of 4 days, AcOH-water (100:1, 404 ml). The organic layer was separated, the aq. layer extracted with petroleum ether (b.p. 40–60°) several times (8 × 100 ml), the combined extracts (~1000 ml) dried and evaporated. The viscous residue was triturated with methanol (12 ml) left overnight in the ice-chest and the crystals collected to give **3**, yield 35 g (32%); m.p. 64–66° (lit.[17] 62–64°). IR: ν_{max} (KBr) (cm^{-1}): 1640 (C=C), 1504, 1333 (NO_2); NMR δ_{CCl_4}: 1.18 (s, C–CH_3, 6 protons), 4.05 (bridgehead proton shifted downfield due to proximate nitro group), 6.7 (s, olefinic proton).

Reduction of ω-nitrocamphene **3** *with chromous chloride-isolation of 3-hydroxy 4,4-dimethyl bicyclo(3,2,1)octan-2-one* **8**

(a) *Preparation of chromous chloride.* Amalgamated zinc dust was prepared by shaking vigorously for 5 min a suspension of zinc dust (120 g) and a soln of $HgCl_2$ (9.6 g) in water–HCl (20:1, 126 ml). The product was allowed to settle and the supernatant liquid decanted. Dil. HCl (250 ml, 1N) was added to the amalgam and the mixture transferred to a 3 necked flask (2 l. capacity) equipped with a stirrer and nitrogen inlet. Under nitrogen and vigorous stirring, chromic chloride hexahydrate (60 g) was introduced in small portions. After completion of addition, the mixture was left stirred for additional 0.5 h. This soln was used immediately for the following experiment.

(b) *Reaction of ω-nitrocamphene with chromous chloride.* Under nitrogen, a soln of ω-nitrocamphene (6 g, 0.33 mole) in freshly distilled and purified THF (200 ml) was mixed with chromous chloride soln from (a). Reduction was rapid as evidenced by the formation of the green colour Cr(III) species. The reaction mixture was refluxed for 3 h under nitrogen, THF distilled off, the residue was allowed to attain room temp. and extracted with chloroform (500 ml). The organic extract was dried ($MgSO_4$) and solvent evaporated to give **8** as a viscous liquid; essentially single product (TLC). Yield 4.37 g (78%); b.p. (110–120°/5 mm). Yield of pure product 3.39 g (68%). TLC: Single spot (R_f: 0.5, benzene); (Found: C, 71.53, H, 9.65, Calc. for $C_{10}H_{16}O_2$ (M. wt., 168); C, 71.42; H, 9.52%). IR ν_{max} (neat) (cm^{-1}): 3436 (OH), 1709 (C=O); NMR: δ_{CCl_4}: 0.75, 1.15 (s, C–CH_3, 6 protons), 1.35–2.25 (methylene and bridgehead protons), 3.65 (broad, hydroxyl proton), 3.8 (s, non-bridgehead *tert.* proton).

Oxidation of 3-hydroxy-4,4-dimethylbicyclo(3,2,1)octan-2-one **8** *to 4,4-dimethylbicyclo(3,2,1)octan-2,3-dione* **9**. A soln of **8** (0.672 g, 0.004 mole) in acetic acid: water: methanol (2:2:0.5, 4.5 ml) was mixed with cupric acetate monohydrate (1.60 g, and the suspension refluxed for 0.5 h. The reaction mixture was filtered, washed with small amounts of MeOH (2 ml) and the yellow filtrate was diluted with ether, washed with sat $NaHCO_3$, water, dried ($MgSO_4$) and evaporated to give 0.523 g (78%) of pure **9**. Distillation of **9** at 105°/1.5 mm gave pure dione (TLC), yield 0.370 g (55%). The distillate crystallized on standing and recrystallization from hexane gave the product, m.p. 48–50°. TLC: Single spot (R_f: 0.45, benzene); (Found: C, 72.14; H, 8.09. Calc. for $C_{10}H_{14}O_2$ (M. wt., 166); C, 72.3; H, 8.43%). IR: ν_{max} (KBr) (cm^{-1}): 1720, 1750 (C=O); NMR: δ_{CCl_4}: 1.1, 1.14 (s, C–CH_3, 6 protons), 1.2–2.6 (methylene and bridgehead protons), 2.98 (broad, COCH-bridgehead proton).

Acetylation of 3-hydroxy-4,4-dimethylbicyclo(3,2,1)octan-2-one. A soln of **8** (0.475 g, 0.0028 mole) in Ac_2O (2 ml) was treated with pyridine (5 drops) and the mixture left aside overnight. Solvents were removed *in vacuo* to give 0.550 g (93%) of essentially pure **10** which on distillation (165–170°/1 mm) gave 0.450 g (76%) of pure acetoxy compound. (Found: C, 68.89; H, 8.35. Calc. for $C_{12}H_{18}O_3$ (M. wt., 210): C, 68.57; H, 8.57%). IR: ν_{max} (neat) (cm^{-1}): 1725, 1750 (C=O); NMR δ_{CCl_4}: 1.19, 1.06 (s, C–CH_3, 6 protons), 1.2–2.2 (methylene and bridgehead protons), 2.08 (s, $COCH_3$), 2.7 (broad, COCH-bridgehead proton), 4.9 (s, non-bridgehead *tert.* proton).

Reaction of ω-nitrocamphene **3** *with fuming hydrobromic acid preparation of exo - 2 - bromo - 7,7 - dimethylbicyclo(2,2,1)heptane - 1 - bromoaldoxime* **16**

(a) *Fuming hydrobromic acid.* To a magnetically stirred mixture of tetralin (45 g) and pure iron filings (5 g) in a flask immersed in a water bath held at 40° and equipped with a dropping funnel and a glass outlet tube, was added in drops, Br_2 (215 g). HBr gas was passed successively through tetralin and water (40 ml) cooled in ice. HBr was passed until brown fumes could be seen coming out and there was a weight increase amounting to 120 g. The reagent was used without delay.

(b) *Reaction of ω-nitrocamphene* **3** *with fuming hydrobromic acid.* Finely powdered ω-nitrocamphene (10 g, 0.055 mol) was introduced in one lot into fuming HBr (100 g) and cooled in crushed ice. The reaction mixture was allowed to attain room temp. and then left aside with occasional shaking for 24 h. Initially the major portion became a hard solid, which consequently turned granular. This was filtered, washed with water and dried to give crude material (14.5 g), which on crystallization from benzene–hexane (1:1) gave colourless thick crystals of **16**, yield 5.00 g (28%), m.p. 132–34° (lit.[14] 132–33°). TLC: Single spot (R_f: 0.75, benzene, EtOAc (1:1)); (Found: C, 36.64; H, 4.64; N, 4.34. Calc. for $C_{10}H_{15}NOBr_2$ (M. wt. 325): C, 36.92; H, 4.61; N, 4.30%); IR: ν_{max} (KBr) (cm^{-1}): 3380 (OH), 1635 (C=N); NMR: δ_{CDCl_3}: 1.16, 1.5 (s, C–CH_3, 6 protons), 1.7–2.5 (methylene and bridgehead protons); 4.35 (9, non-bridgehead *tert.* proton); 7.8 (s, hydroxyl proton).

Compound **16** could also be prepared in quantitative yeilds by reaction of **14** with fuming HBr.

Preparation of exo - 2 - bromo - 7,7 - dimethylbicyclo(2,2,1)heptane - 1 - nitrile oxide **14**. Under dry conditions, to an ice cooled and stirred soln of **16** (1.03 g, 0.0032 mole) in dry ether (50 ml) was added in drops a soln of triethyl amine (0.350 g, 0.0034 mole) in dry ether (25 ml). The precipitated triethylammonium bromide was filtered and solvents evaporated to give **14**, m.p. 120–22°; yield 0.73 g (93%). Crystallization from hot hexane gave crystals m.p. 123–125°. This nitrile oxide can be stored indefinitely. TLC: Single spot (R_f: 0.6, benzene). (Found: C, 49.32; H, 6.04; N, 5.74. Calc. for $C_{10}H_{14}NOBr$ (M. wt., 244): C, 49.18; H, 5.74; N, 5.74%). IR: ν_{max} (KBr) (cm^{-1}): 2275 ($C{\equiv}N^+$–O^-), 1330 (–N–O); NMR: δ_{CDCl_3}: 1.1, 1.4 (s, C–CH_3, 6 protons), 1.5–2.5 (methylene and bridgehead protons), 4.15 (q, non-bridgehead *tert.* proton).

Reaction of **14** *with ammonia-isolation of exo - 2 - bromo - 7,7 - dimethylbicyclo(2,2,1)heptane - 1 - amidoxime* **17**. Ammonia was passed through an ice cooled soln of **14** (0.13 g, 0.0053 mole) in dry ether (5 ml) for 0.25 h. An aliquot taken after 5 min showed large amounts of unchanged **14** (TLC). The reaction mixture was left aside overnight, concentrated and the crystals of **17** collected, m.p. 156° (dec); yield 0.155 g (97%); TLC: Single spot (R_f: 0.20, benzene). (Found: C, 45.98; H, 6.6; N, 10.89. Calc. for $C_{10}H_{17}N_2OBr$ (M. wt., 261): C, 46.15: H, 6.54; N, 10.7%). IR: ν_{max} (KBr) (cm^{-1}): 3300 (NH_2), 3160 (OH), 1650 (C=N), 1575 (NH_2); NMR: δ_{CDCl_3}: 1.14, 1.54 (s, C–CH_3, 6 protons), 1.65–2.65 (methylene and bridgehead protons), 4.34 (q, non-bridgehead *tert.* proton).

Reaction of **14** *with dimethyl acetylene dicarboxylate.* Dry ether soln of **14** (0.244 g, 0.001 mole, 5 ml) and dimethyl acetylene dicarboxylate (0.142 g, 0.001 mole, 5 ml) were mixed and kept at room temp. for 20 h. Removal of solvents gave a quantitative yield of essentially pure (TLC) adduct **18** which was distilled, b.p. 120–25°/2 mm. Yield: 0.316 g(81%). TLC: single spot (R_f: 0.40, benzene). (Found: C, 49.87; H, 5.34; N, 3.82. Calc. for $C_{16}H_{20}NO_5Br$ (M. wt., 386): C, 49.7, H, 5.2; N, 3.62%). IR: ν_{max} (neat) (cm^{-1}): 1745, 1730 (C=O); NMR: δ_{CCl_4}: 1.22, 1.49 (s, C–CH_3, 6 protons); 1.65–2.4 (methylene and bridgehead protons), 3.79, 3.9 (s, $COOCH_3$, protons), 4.6 (q, non-bridgehead, *tert.* proton).

Pyrolysis of the nitrile oxide **14**—*isolation of exo - 2 - bromo - 7,7 - dimethylbicyclo(2,2,1)heptane - 1 - isocyanate* **19**. Under dry conditions a soln of **14** (0.300 g, 0.0012 mole) in dry xylene (3 ml) was refluxed for 4 h. Solvents were removed under reduced pressure and the residue distilled to give **19**, b.p. 130°/2 mm; yield 0.130 g (43%). The clear liquid crystallized on standing, m.p. 80–82°. TLC: Single spot (R_f: 0.80, benzene); (Found: C, 49.4, H, 5.8. Calc. for $C_{10}H_{14}NOBr$ (M. wt. 244): C, 49.18; H, 5.74%); IR: ν_{max} (CCl_4) (cm^{-1}): 2260 (N=C=O); NMR: δ_{CCl_4}: 1.04, 1.3 (s, C–CH_3, 6 protons); 1.35–2.45 (methylene and bridgehead protons), 4.2 (q, non-bridgehead *tert.* protons).

Reaction of the nitrile oxide **14** *with methanolic potassium hydroxide–isolation of 2 - methoxy - 3,3 - dimethylbicyclo(2,2,1)-heptane - 2 - methoxyaldoxime* **20**. An ice cooled and stirred dry MeOH soln of the nitrile oxide **14** (0.150 g, 0.006 mole, 2 ml) was mixed with saturated dry methanolic KOH (3 ml). The reaction mixture was left aside for 2 days. The solvent was removed under reduced pressure without heating, the residue treated with crushed ice and extracted with ether (2 × 25 ml), washed with water, dried ($MgSO_4$) and evaporated. Crystallization from benzene–hexane gave pure **20**, m.p. 102°; yield 0.09 g (65%). TLC: Single spot (R_f: 0.72, benzene, EtOAc (1:1)). (Found: C, 63.10; H, 9.33. Calc. for $C_{12}H_{21}NO_3$ (M. wt., 227): C, 63.43; H, 9.2%); IR: ν_{max} (KBr) (cm^{-1}): 3300 (OH), 2860 (OCH_3), 1650 (C=N), 1270, 1070 (=C–O–C); NMR: δ_{CCl_4}: 1.0, 1.05 (s, C–CH_3, 6 protons), 1.15–2.15 (methylene and bridgehead protons), 3.15 (s, C–OCH_3, 3 protons), 4.12 (s, N=C–OCH_3, 3 protons), 7.8 (hydroxyl proton).

Reaction of **17** *with boiling water—isolation of exo - 2 - hydroxy - 3,3 - dimethylbicyclo(2,2,1)heptane - 2 - amidoxime* **21**. An aq. suspension of **17** (0.300 g, 0.001 mole, 2 ml) was refluxed for 0.25 h. The clear reaction mixture was cooled, made basic with aq. ammonia and the precipitated white solid collected. Crystallization from absolute EtOH gave **21**, m.p. 178–81°; yield 0.12 g (53%). (Found: C, 60.39; H, 9.26; N, 14.29. Calc. for $C_{10}H_{18}N_2O_2$ (M. wt. 198): C, 60.60; H, 9.08; N, 14.1%); IR: ν_{max} (KBr) (cm^{-1}): 3300 (NH_2), 3160 (OH), 1640 (C=N), 1575 (NH_2); NMR: $\delta_{(TFA)}$: 1.2, 1.3 (s, C–CH_3, 6 protons), 1.5–2.5 (methylene and bridgehead protons), 2.65 (s, bridgehead *tert.* proton), 7.5 (broad, hydroxyl protons).

Reaction of **17** *with aqueous silver nitrate—isolation of exo - 2 - hydroxy - 3,3 - dimethyl - bicyclo(2,2,1)heptane - 2 - amidoxime* **21**. To stirred aq. $AgNO_3$ (0.3 g, 0.0017 mole, 3 ml) was added at room temp. **17** (0.300 g, 0.001 mole). AgBr precipitated immediately. After 0.25 h excess $AgNO_3$ was removed by addition of dil. HCl (6N, 1 ml). The reaction mixture was filtered, neutralized with sat $NaHCO_3$, sat NaCl and extracted with ether. The ether extract was dried ($MgSO_4$) and evaporated to give **21**, yield 0.06 g (26%). Crystallization from EtOH gave pure material, m.p. 181°. The IR was identical with the compound obtained in the previous experiment and the mixed m.p. was undepressed.

ω-Nitroso camphene via electrophilic substitution of camphene

Isolation of 3a,4,5,6,7,7a - *hexahydro* - 3a,6 - *methano* - 8,8 - *dimethylbenzisoxazole* **22**. To ice-salt cooled (−5°) and stirred mixture of conc. H_2SO_4 (98%, 100 ml) and light petroleum (65–70°, 12 ml) was added solid $NaNO_2$ (11.2 g, 0.1623 mole) in batches, maintaining the temp. below −5°. Subsequently a soln of camphene (10 g, 0.0733 mole) in light petroleum (65–70°, 25 ml) was added to such a rate that the temp. did not rise above −5°. After additional 1 h stirring, the mixture was poured on crushed ice, filtered, washed with dilute ammonia and dried to yield 5.5 g of crude isoxazoline **22**. Sublimation gave pure product: yield 3.650 g (33%), m.p. 210° (dec). (Found: C, 72.95; H, 9.20; N, 8.73. Calc. for $C_{10}H_{15}NO$ (M. wt., 165): C, 72.72; H, 9.09; N, 8.48%). UV: λ_{max}: 224 nm; IR: ν_{max} (KBr) (cm^{-1}): 1563 (C=N–O); NMR: δ_{CCl_4}: 0.95, 1.00 (gem-dimethyl), 4.20 (d,d endo proton), 7.00 (s, isoxazoline proton).

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