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# Stereochemistry in the Oxidation of Primary Amines to Nitro Compounds by Dimethyldioxirane[1]

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**Abstract:** Oxidation of the chiral amines, (+) and (-)-isopinocampheylamine, with dimethyldioxirane (**1**) gives the corresponding nitro compounds with retention of configuration at the amine-bearing carbon atom. When lower amounts of **1** are used in the oxidation the amines give the nitroso dimers as the major products. Treatment of the nitroso dimer from the (-)-amine with additional **1** gave the same nitro compound as obtained from the amine oxidation. To further indicate that no racemization occurs during the amine oxidation we have synthesized the oxime of the nitroso intermediate and shown that it does not tautomerize under the reaction conditions.
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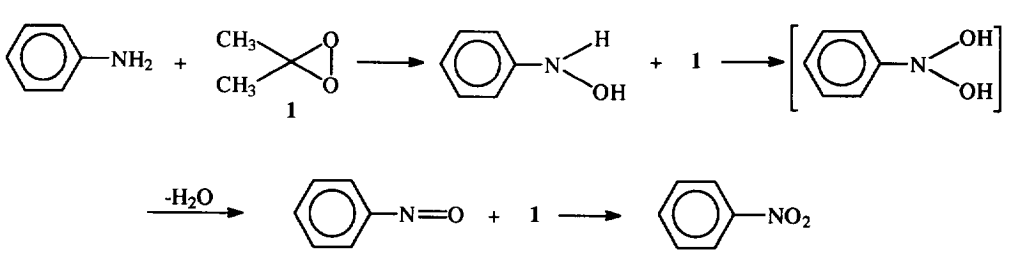
## INTRODUCTION

Since our first report[2] that dimethyldioxirane **1** converts primary amines to nitro compounds in a rapid, high yield process, a number of similar reports[3-14] on the oxidation of primary amines by **1** have appeared. The mechanism of this oxidation has received little attention however. In the earlier report[2] we suggested that the reaction proceeds through a series of O atom transfers (Scheme 1). Because the intermediate compounds produced in this process can react with each other and the starting amine, we subsequently showed[3] that when the nitro compound is the desired product the amine should be added to an excess of **1**. Primary aliphatic amines have been reported[6] to give mixtures of products including oximes and dimers of the intermediate nitroso compounds along with the nitro compounds in some cases.

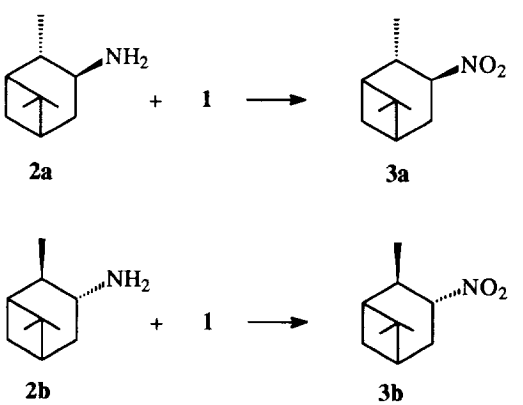



Scheme 1

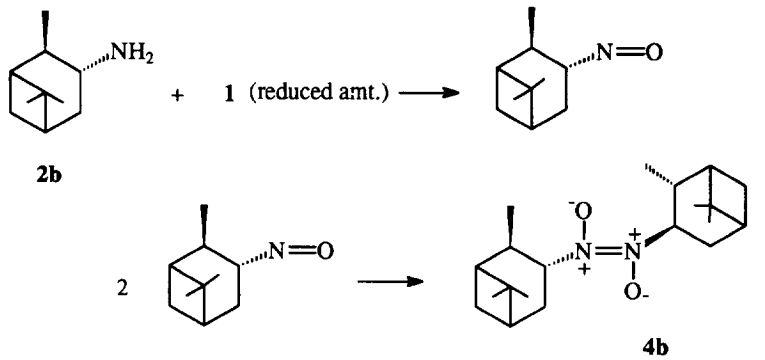
*A priori* the individual O atom transfers (Scheme 1) involved in the production of the nitro compound could involve an insertion reaction of **1** into an N-H bond in a manner analagous to the C-H insertion reaction[15] of **1**. Alternatively, since **1** is known to be an electrophilic reagent, the reaction could proceed to give N-oxy type intermediates which could quickly rearrange to, for example, a hydroxylamine in the first step. In the case of a hydrazine it has been suggested[16] that the first step in the reaction with **1** involves electron transfer from the hydrazine to the dioxirane to give radical type chemistry. This suggestion is based on the earlier observation[17] that methyl(trifluoromethyl)dioxirane undergoes an electron transfer reaction with a nitroxide. On the other hand Adam and Golsch have shown[18] that the rates of reaction of a series of nitrogen nucleophiles with **1** are linearly related to the rates of the same materials in nucleophilic displacement reactions with methyl iodide. These results are not consistent with an electron transfer mechanism.

## RESULTS AND DISCUSSION

In the current work we have oxidized separately the enantiomers of isopinocampheylamine, **2a** (+) and **2b** (-), to the nitro derivatives, **3a** and **3b**, using **1** (Scheme 2). The reaction proceeds in quantitative or near quantitative yield and gives a single nitro compound in each case. GLC analysis using a chiral column indicated that the products **3a** and **3b** are enantiomers. Since tautomerization of the nitroso compound to the oxime[6] would represent a challenge to the configurational stability of the carbon bearing the amino group we have also carried out the oxidation with a reduced amount of **1**. Under these conditions the blue color of the nitroso compound is observed to persist providing maximum opportunity for tautomerization (and racemization) to occur. Under these conditions **2a** gives a mixture of **3a** (22 %) and the nitroso dimer **4a** (78 %), while **2b** gives **3b** (17 %) plus dimer **4b** (83 %) (Scheme 3).

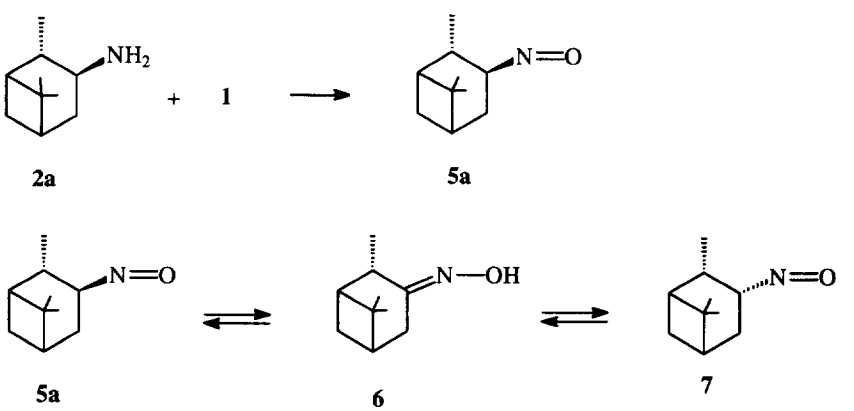



Scheme 2




Scheme 3

Analysis of the nitro products on a chiral GLC column indicated that both of the oxidations had given the same single enantiomer as observed in the earlier oxidations with excess **1** indicating that configurational integrity had been retained at the amine bearing-carbon atoms. This conclusion is further supported by the fact that oxidation of each amine gave a single nitro product. The structures of the amines are such that any racemization at the carbon bearing the amino group would have led to the formation of diastereomers. To further support the argument that racemization has not occurred at C-3 in **2a** we have synthesized oxime **6**. This oxime is the product of tautomerization of nitroso compound **5a** and, if present, would permit access to the diastereomeric nitroso compound **7** (Scheme 4). We then showed that **6** does not tautomerize under the reaction conditions. When **2a** and **6** are co-oxidized under the reaction conditions we find that no oxidation of **6** occurs until **2a** is completely converted to nitro compound **3a**. Furthermore when **6** is separately oxidized by **1** it gives a mixture of products with the corresponding ketone predominating. Thus, we conclude that no **6** was formed under our reaction conditions and that no access to **7** was available.




Scheme 4

In a separate experiment it was shown that **4b** is readily converted to **3b** when treated with additional **1**. The X-ray crystal structures of the nitroso dimers indicate that they have *trans* stereochemistry about the N-N

bond. Fig. 1 shows the X-ray crystal structure for dimer **4b**. This appears to be the first reported X-ray crystal structure of a chiral nitroso dimer. The two halves of the dimer are related by a crystallographic two fold axis located on the N=N bond. Even though both optically pure enantiomers were crystallized and their X-ray structures were determined, attempts to elucidate absolute configuration were not successful. Here we have reported the structure of isomer **4b**.

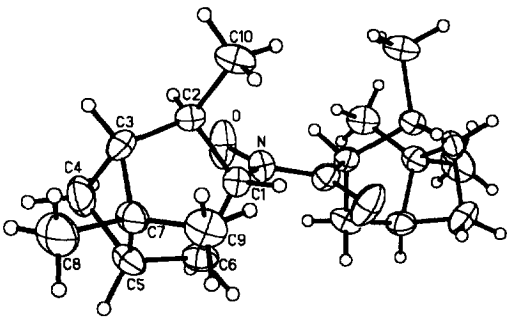



Fig. 1. X-ray Crystal Structure of **4b**

These results are consistent with either of the two mechanisms described above, that is, a series of N-H insertion reactions or a succession of O transfers to the nitrogen followed by H transfer. They are not consistent with the intervention of tautomerization in an intervening nitroso compound. Given the earlier results of Adam and Golsch[18] we favor a mechanism involving a succession of nucleophilic displacements of the nitrogen compounds on **1**. We believe that a radical process is unlikely, as is an N-H bond insertion reaction of **1**.

## EXPERIMENTAL

*General.* $^{1}H$ and $^{13}C$ NMR spectra were recorded on a Varian XL-300 NMR spectrometer with $CDCl_3$ as solvent. All chemical shift data are reported in ppm or δ values downfield from TMS. The multiplicities of the $^{13}C$ NMR signals were determined by the attached proton test (APT) pulse sequence.Optical rotations were recorded on a Rudolph Research automatic polarimeter Aotopol III. Specific rotations, $[\alpha]_D$, are reported in degrees per decimeter at 22°C at the sodium D line (589 nm) (unless stated otherwise), and the concentration (c) is given in grams per 100 mL in the specified solvent. Electron impact and chemical ionization mass spectra were recorded (70 eV ionizing voltage) on a Hewlett-Packard 5988A twin EI and CI quadrupole mass spectrometer connected to a Hewlett-Packard 5890A gas chromatograph fitted with a Hewlett-Packard 12 m X 0.2 mm X 0.33 μm Ultra-1 (cross-linked methyl silicone) column. UV-VIS spectra were obtained on a Hitachi U-3110 UV-VIS spectrophotometer. Infrared spectra were recorded as thin films between KBr disks or as solids in KBr pellets on a Perkin-Elmer Model 1600 FT-IR spectrometer. Melting points were determined on a Dynamics Optics AHT 713921 hot-stage apparatus and are uncorrected. Chromatographic separations on the chromatotron Model 8924 (Harrison Research) were accomplished using 1 mm Kieselgel 60 $PF_{254}$ gypsum

plates. Gas chromatography was performed on a Perkin Elmer Sigma 2000 gas chromatograph using a flame ionization detector, a J and W Scientific fused silica DB-210 capillary column (30 m X 0.318 mm; film thickness 0.5 μm), and He as carrier gas. The chromatograph was interfaced with a Shimadzu Chromatopac C-R3A integrator. Chiral GLC analysis was performed isothermally using a CYCLODEX-B chiral capillary column (30 m X 0.25 mm; film thickness (0.25 μm). Preparative GLC was performed on a Varian Aerograph Model 700 gas chromatograph employing a dual rhenium-tungsten filament thermal conductivity detector and using He as carrier. The column used was a 12 ft X 3/8 in aluminum column packed with 8% SF-96 methyl silicone on chromosorb G 60/80 mesh. Microanalyses were performed by the Atlantic Microlab, Inc., Norcross, GA.

*Materials and Reagents.* Acetone (Fisher reagent grade) was fractionally distilled over anhydrous potassium carbonate. Oxone (DuPont), $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$, was obtained from Aldrich Chemical Co. and used as such. (+) and (-) - Isopinocampheylamines (98% purity) and (+)- isopinocampheol were obtained from Aldrich Chemical Co. and used as received. The dimethyldioxirane solution in acetone was prepared according to the literature procedure[19] and was assayed for dioxirane content using phenyl methyl sulfide and the GLC method or concentration was determined using a calibration curve of concentration of **1** versus UV absorbance at 335 nm.

*(+)-2,6,6-Trimethyl-3-nitro-bicyclo[3.1.1]heptane (**3a**).* A solution of (***1S, 2S, 3S, 5R***)-(+)-isopinocampheylamine (**2a**) (0.11 g, 0.7176 mmol) in $CH_2Cl_2$ (20 mL) was added dropwise to a magnetically stirred solution of **1** (0.073 M) in acetone (43 mL, 2.87 mmol) over a period of 20-30 min. The reaction mixture was stirred at room temperature for another 30 min to give a pale yellow solution. The progress of the reaction was monitored by GLC which indicated the formation of one product. The solvent was removed on a rotovap to give a pale yellow oily liquid and traces of water. The residue was dissolved in $CH_2Cl_2$ and dried with sodium sulfate. Evaporation of the $CH_2Cl_2$ *in vacuo* gave **3a** as a pale yellow liquid (0.1313 g, 100%). An analytically pure sample was collected by preparative GLC as a colorless liquid: $[\alpha]_D^{22}$+29.5 (*c* = 1, $CH_2Cl_2$); IR (neat, $cm^{-1}$): 2922(s), 1554(s), 1472(m), 1452(m), 1374(s), 1317(m), 1278(m), 1155(w), 950(m), 930(m), 840(m), 724(m); $^1H$ NMR (300 MHz, $CDCl_3$): δ 0.94 (s, 3H, **$CH_3$**- at C-6), 1.23 (d, **J** = 7.32 Hz, 3H, **$CH_3$**- at C-2), 1.25 (d, J = 9.57 Hz, 1H), 1.26 (s, 3H, **$CH_3$**- at C-6), 1.85-1.95 (m, 1H), 2.00-210 (m, 1H), 2.35-2.50 (m, 2H), 2.50-2.70 (m, 2H), 4.84 (ddd, J = 10.25, 6.44, and 5.73 Hz, 1H, -**CH**-$NO_2$ at C-3); $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 21.06 (**$CH_3$**-), 23.31 (**$CH_3$**-), 27.39 (**$CH_3$**-), 32.72 (-**$CH_2$**-), 32.78 (-**$CH_2$**-), 38.39 (> **C**$(CH_3)_2$), 40.58 (-**C**H-), 42.51 (-**C**H-), 47.0 (-**C**H-), 86.30 (-**C**H-$NO_2$, C-3); MS(EI, 70eV): m/z 153 (0.3), 152 (3), 137 ($M^+$-$NO_2$, 2), 136 (4), 121 (27), 107 (16), 93 (100), 81 (74), 69 (56), 55 (57), 43 (71), 41 (51); MS (CI, methane) did not show the M+H or M peak; Calcd for $C_{10}H_{17}NO_2$: 183.25. *Anal.* Calcd for $C_{10}H_{17}NO_2$: C, 65.54; H, 9.35; N, 7.64. Found: C, 65.70; H, 9.39; N, 7.48. Chiral GLC of the product at 150°C showed only one peak at 15.0 min.

*(-)-2,6,6-Trimethyl-3-nitro-bicyclo[3.1.1]heptane (**3b**).* The above procedure was followed using a solution of (***1R, 2R, 3R, 5S***)-(-)-isopinocampheylamine (**2b**) (0.104 g, 0.6785 mmol) in $CH_2Cl_2$ (20 mL) and a solution of **1** (0.07 M) in acetone (45 mL, 2.714 mmol). After the usual workup **3b** was isolated as a pale yellow liquid (0.1194 g, 96 %). An analytically pure sample was collected by preparative GLC as a colorless

liquid: $[\alpha]_D^{22}$ - 29.8 (*c* = 1, $CH_2Cl_2$); IR (neat, $cm^{-1}$): 2922(s), 1553(s), 1472(m), 1452(m), 1374(s), 1347(m), 1317(m), 1278(m), 1155(w), 950(m), 930(m), 840(m), 724(m); $^1H$ NMR (300 MHz, $CDCl_3$): δ 0.94 (s, 3H, **$CH_3$**- at C-6), 1.23 (d, J = 7.32 Hz, 3H, **$CH_3$**- at C-2), 1.25 (d, J = 9.52 Hz, 1H), 1.26 (s, 3H, **$CH_3$**- at C-6), 1.85-1.95 (m, 1H), 2.00-2.10 (m, 1H), 2.35-2.50 (m, 2H), 2.50-2.70 (m, 2H), 4.838 (ddd, J = 10.28, 6.48, and 5.72 Hz, 1H, -**CH**-$NO_2$ at C-3); $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 21.06 (**$CH_3$**-), 23.32 (**$CH_3$**-), 27.39 (**$CH_3$**-), 32.72 (-**$CH_2$**-), 32.78 (-**$CH_2$**-), 38.39 (> **C**($CH_3$)$_2$), 40.57 (-**CH**-), 42.52 (-**CH**-), 46.98 (-**CH**-), 86.30 (-**CH**-$NO_2$, C-3); MS (EI, 70 eV): m/z 152 (0.2), 137 ($M^+$ -$NO_2$, 2), 136 (4), 121 (26), 107 (15), 105 (10), 93 (100), 81 (69), 67 (51), 55 (54), 41 (63); MS (CI, methane) did not show the M+H or M peak; Calcd for $C_{10}H_{17}NO_2$: 183.25. Anal Calcd. for $C_{10}H_{17}NO_2$: C, 65.54; H, 9.35; N, 7.64. Found: C, 65.58; H, 9.33; N, 7.63. Chiral GLC analysis of the sample at 150°C showed only one peak at 14.6 min.

*(-)-C-Nitroso Dimer (**4b**).* To a magnetically stirred solution of ***(1R, 2R,3R,5S)***-(-)isopinocampheylamine (0.05 g, 0.326 mmol) in $CH_2Cl_2$ (15 mL) was added dropwise a solution of **1** (0.055 M) in acetone (12 mL, 0.652 mmol) over a period of 5 min during which time the color of the solution changed from colorless to blue. The reaction mixture was stirred for 30 min to give a colorless solution. The solvent was removed on the rotovap to give a colorless solid and traces of water. The residue was dissolved in a mixture of hexane and $CH_2Cl_2$ and dried with sodium sulfate. Evaporation of the solvent gave a colorless crystalline solid (0.055 g). $^1H$ NMR analysis of the crude residue indicated the presence of **3b** (22%) and the dimer **4b** (78%). Purification of the residue on the chromatotron using hexane/$CH_2Cl_2$ (55:45) as the eluent gave a pure sample of the dimer (0.029 g, 54 %) as a colorless crystalline solid, mp 120-122°C; $[\alpha]_D^{26}$ - 49.23 (*c* = 0.65, $CH_2Cl_2$); IR (KBr, $cm^{-1}$): 2984(s), 2927(s), 1458(s), 1409(ms), 1286(m), 1272(m), 1210(vs), 1200(s), 1150(m), 1008(m), 686(s), 544(m); $^1H$ NMR (300 MHz, $CDCl_3$): δ 1.04 (s, 3H, **$CH_3$**-), 1.10 (d, J = 7.32 Hz, 3H, **$CH_3$**-), 1.26 (s, 3H, **$CH_3$**-), 1.29 (d, J = 10.0 Hz, 1H), 1.80-210 (m, 3H), 2.30-2.45 (m, 1H), 2.45-2.65 (m, 1H), 2.65-2.85 (m, 1H), 5.80 (dt, J = 10.50 and 6.28 Hz, 1H, -**CH**-N= at C-3); $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 21.00 (**$CH_3$**-), 23.28 (**$CH_3$**-), 27.70 (**$CH_3$**-), 31.35 (-**$CH_2$**-), 32.72 (-**$CH_2$**-), 38.62 (>**C**($CH_3$)$_2$), 39.64 (-**CH**-), 40.80 (-**CH**-), 47.27 (-**CH**-), 65.61 (-**CH**-N=); MS (EI, 70 eV): m/z 335 (M+1, 1), 334 ($M^+$, 4), 168 (8), 167 (2), 152 (9), 138 (36), 137 (100), 109 (18), 96 (35), 93 (42), 83 (51); Calcd. for $C_{20}H_{34}N_2O_2$: 334.50. Anal Calcd. for $C_{20}H_{34}N_2O_2$: C, 71.81; H, 10.25; N, 8.37. Found: C, 71.77; H, 10.26; N, 8.32.

*(+)-C-Nitroso Dimer (**4a**).* The above procedure was followed using a solution of ***(1S,2S,3S,5R)***-(+)-isopinocampheylamine (**2a**) (0.110 g, 0.718 mmol) in $CH_2Cl_2$ (10 mL) and a solution of **1** (0.071 M) in acetone (22.5 mL, 1.435 mmol). After the usual workup a colorless solid was obtained (0.118 g). $^1H$ NMR analysis of the crude product indicated the presence of **3a** (10%) and dimer **4a** (90%). Purification of the product on the chromatotron using hexane/$CH_2Cl_2$ (55:45) as the eluent gave a pure sample of **4a** (0.081 g, 74%) as a colorless crystalline solid, mp 120-122°C; $[\alpha]_D^{23}$ + 49.3 (*c* = 1.0, $CH_2Cl_2$); IR (KBr, $cm^{-1}$): 2983(s), 2927(s), 1458(s), 1408(ms), 1382(ms), 1286(m), 1272(m), 1210(vs), 1200(s), 1150(m), 1008(m), 686(s), 544(m); $^1H$ NMR (300 MHz, $CDCl_3$): δ 1.04 (s, 3H, **$CH_3$**-), 1.10 (d, J = 7.33 Hz, 3H, **$CH_3$**-), 1.26 (s, 3H, **$CH_3$**-), 1.29 (d, J = 10.0 Hz, 1H), 1.80-2.10 (m, 3H), 2.30-2.45 (m, 1H), 2.45-2.65 (m, 1H), 2.65-2.85, (m,1H), 5.80 (dt, J = 10.30 and 6.30 Hz, 1H, -**CH**-N= at C-3); $^{13}C$ NMR (75 MHz, $CDCl_3$): δ 21.00 (**$CH_3$**-), 23.29 (**$CH_3$**-), 27.72 (**$CH_3$**-), 31.36 (-**$CH_2$**-), 32.74 (-**$CH_2$**-), 38.64 (>**C**($CH_3$)$_2$), 39.66 (-**CH**-), 40.82 (-**CH**-), 47.31 (-**CH**-), 65.62 (-**CH**-N=); MS (EI, 70 eV): m/z 335 (M+1, 1), 334 ($M^+$, 3), 168(4), 167(1), 152(2),

138(12), 137(100), 109(7), 95(9), 93(35), 83(20); Calcd. for $C_{20}H_{34}N_2O_2$: 334.50. Anal Calcd. for $C_{20}H_{34}N_2O_2$: C, 71.81; H, 10.25; N, 8.37. Found: C, 71.81; H, 10.22; N, 8.35.

*Reaction of Dimer **4b** with Dimethyldioxirane.* To a magnetically stirred solution of **2b** (0.093 g, 0.6067 mmol) in acetone was added dropwise a solution of **1** (0.068 M) in acetone (18 mL, 1.22 mmol) over a period of 5 min during which time the color of the solution changed from colorless to blue. The reaction mixture was stirred for 60 min to give a colorless solution. The reaction mixture was worked up as before to a residue containing **3b** (17%) and dimer **4b** (83%). The residue was reacted with additional **1** (1.22 mmol). The reaction solution was stirred for 24 h to give a yellow solution. Workup of this solution gave 0.0466 g (42 %) of **3b** which was identical in all respects to that described in the synthesis given above.

*(+)-2,6,6-trimethyl-bicyclo[3.1.1]heptan-3-one oxime* (**6**). A solution of (***1S,2S,3S,5R***)-(+)-isopinocampheol (0.550 g, 3.566 mmol) in acetone (10 mL) was added dropwise to a magnetically stirred solution of dimethyldioxirane (0.074 M) in acetone (50 mL, 3.70 mmol). The reaction mixture was stirred at room temperature for 8 h to give a pale yellow solution. The solvent was removed on the rotovap to give a pale yellow oily liquid. The residue was dissolved in $CH_2Cl_2$ and dried with sodium sulfate. Evaporation of the $CH_2Cl_2$ *in vacuo* gave (-)-(***1S,2S,5R***)-2,6,6-trimethyl-bicyclo[3.1.1]heptan-3-one as a pale yellow liquid (0.540 g, 99%). An analytically pure sample was collected by preparative GLC as a colorless liquid: $[\alpha]_D^{25}$ - 12.2 ($c$ = 1.15, $CH_2Cl_2$) (lit.[20] $[\alpha]_D^{25}$ - 12.6 (neat)); $^1$H NMR (300 MHz, $CDCl_3$): d 0.87 (s, 3H, **$CH_3$**- at C-6), 1.19 (d, J = 10.30 Hz, 1H), 1.21 (d, J = 7.35 Hz, 3H, **$CH_3$**- at C-2), 1.31 (s, 3H, **$CH_3$**- at C-6), 2.01-2.09 (m, 1H), 2.09-2.16 (m, 1H), 2.40-2.56 (m, 2H), 2.57-2.70 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$): d 16.88 (**$CH_3$**-), 21.97 (**$CH_3$**-), 27.06 (**$CH_3$**-), 34.40 (-**$CH_2$**-), 39.00 (-**CH**-), 39.22 (>**C**($CH_3$)$_2$), 44.76 (-**$CH_2$**-), 45.03 (-**CH**-), 51.31 (-**CH**-), 214.84 (**C=O**, C-3) The $^1$H and $^{13}$C NMR spectra were identical with those of the ketone reported in the literature [20,21]; MS(EI,70eV): m/z 153(M+1,1), 152(M$^+$,13), 110(17), 97(31), 95(46), 83(100), 69(92), 55(85), 41(33); Calcd for $C_{10}H_{16}O$: 152.23.

A mixture of (-)-2,6,6-trimethyl-bicyclo[3.1.1]heptan-3-one (0.3715 g, 2.44 mmol), hydroxylamine.HCl (0.225 g, 3.24 mmol) and sodium acetate (0.5 g, 6.1 mmol) in water (10 ml) and methanol (5 ml) was heated at 60-70°C in a water bath for 16 h. The solvent was removed *in vacuo* and the residue was dissolved in water (15 ml) and extracted with $CH_2Cl_2$ (2 X 25 mL). Drying of the $CH_2Cl_2$ layer with sodium sulfate and evaporation of the $CH_2Cl_2$ in *vacuo* gave (+)-2,6,6-trimethyl-bicyclo[3.1.1]heptan-3-one oxime as a pale viscous liquid (0.3614 g, 89%). GLC analysis of the residue indicated the presence of two diastereoisomers (91:9). An analytically pure sample of the major isomer was collected by preparative GLC as a colorless viscous liquid: $[\alpha]_D^{25}$ + 14.2 ($c$ = 3, $CH_2Cl_2$); IR (Neat, cm$^{-1}$): 3279 (br s), 2917(vs), 1644(m), 1470(m), 1385(m), 1371(m), 1264(w), 1226(w), 1094(w), 951(s), 932(s), 882(w), 814(w), 748(m); $^1$H NMR (300 MHz, $CDCl_3$): d 0.91 (s, 3H, **$CH_3$**- at C-6), 0.97 (d, J = 10.20 Hz, 1H), 1.26 (s, 3H, **$CH_3$**- at C-6), 1.29 (d, J = 7.20 Hz, 3H, **$CH_3$**- at C-2), 1.86-1.94 (m, 1H), 1.95-2.04 (m, 1H), 2.38-2.65 (m, 2H), 2.75-3.00 (m, 2H), 8.63 (br s, 1H, **N-OH**); $^{13}$C NMR (75 MHz, $CDCl_3$): d 19.53 (**$CH_3$**-), 21.84 (**$CH_3$**-), 27.33 (**$CH_3$**-), 30.75 (-**$CH_2$**-), 33.39 (-**$CH_2$**-), 37.99 (-**CH**-), 39.02 (>**C**($CH_3$)$_2$), 41.43 (-**CH**-), 46.04 (-**CH**-), 162.04 (**C=N-OH**, C-3); MS(EI,70eV): m/z 168(M+1,1), 167(M$^+$,7), 152(100), 124(12), 111(15), 108(19), 94(17), 79(16), 69(31), 55(41), 41(20); Calcd for $C_{10}H_{17}NO$: 167.24. Anal Calcd. for $C_{10}H_{17}NO$: C, 71.81; H, 10.25; N, 8.37. Found: C, 71.82; H, 10.25; N,

8.30. ***Minor isomer***: $^{13}C$ NMR (75 MHz, $CDCl_3$): d 17.24 (**$CH_3$-**), 22.27 (**$CH_3$-**), 27.42 (**$CH_3$-**), 31.45 (-**$CH_2$-**), 33.23 (-**$CH_2$-**), 38.64 (-**CH-**), 39.02 (>**C**($CH_3$)$_2$), 39.20 (-**CH-**), 45.57 (-**CH-**), 159.91 (**C=N-OH**, C-3); MS(EI,70eV): m/z 167($M^+$,17), 152(88), 124(19), 112(53), 108(28), 94(31), 79(42), 69(85), 55(100), 41(69); Calcd for $C_{10}H_{17}NO$: 167.24.

*Control Reactions Involving (+)-2,6,6-trimethyl-bicyclo[3.1.1]heptan-3-one oxime* (**7**). (1) A solution of oxime **7** (0.041 g, 0.245 mmol) and (***1S,2S,3S,5R***)-(+)-isopinocampheylamine (**2a**) (0.076 g, 0.496 mmol) in $CH_2Cl_2$ (10 mL) was added dropwise to a magnetically stirred solution of dimethyldioxirane (0.074 M) in acetone (33 mL, 2.442 mmol) over a period of 15-20 min. The reaction mixture was analyzed immediately by GLC which indicated the presence of starting oxime and (+)-2,6,6-trimethyl-3-nitro-bicyclo[3.1.1]heptane (**3a**) only. No trace of starting amine and no change in the amount of the oxime was observed in 20 min. The reaction mixture was stirred for additional 30 min. GLC analysis of the reaction mixture indicated the presence of the oxidation products of the oxime. The amount of the oxime was also decreased considerably. GLC analysis of the reaction mixture after 110 min indicated the absence of the oxime. (2) *Reaction of oxime 7 with Dimethyldioxirane*. A solution of **7** (0.018 g, 0.1076 mmol) in acetone (3 ml) was added to a magnetically stirred solution of dimethyldioxirane (0.074 M) in acetone (3 mL, 0.222 mmol). The reaction mixture was stirred at room temperature. GLC analysis of the reaction mixture after 30 min indicated the presence of three products in the ratio 31:28:41. One of the major products was identified as 2,6,6-trimethyl-bicyclo[3.1.1]heptan-3-one (31%). GLC analysis after 3 h indicated no trace of oxime. No attempt was made to identify the remaining two oxidation products. (3) *Attempted tautomerization of 7 in acetone*. A solution of **7** (0.046 g) in acetone was stirred at room temperature for 60 min. the reaction mixture was analyzed by GLC after 60 and 180 min. No change or difference in the GLC trace was observed. The solution remained colorless throughout the experiment. No tautomerization of oxime was observed under these experimental conditions.

*X-ray Diffraction Study of Dimer **4b***. Colorless crystals of the title compound were obtained by recrystallization from acetone at room temperature. Details for the crystal structure determination are given in Table 1. Table 2 gives the atomic coordinates. Bond distances and angles are reported in Table 3. Data reduction was carried out by XSCANS (Siemens Analytical X-Ray, Madison, WI, 1994). SHELXTL 5.0 (Sheldrick, G.M., Siemens Analytical X-Ray, Madison, WI, 1995) was used for structure solution and refinement. The structure was solved by Direct methods and was refined successfully in orthorhombic space group $C222_1$. Full matrix least-squares refinement was carried out by minimizing $w(Fo^2-Fc^2)$. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were refined using appropriate riding model. The absolute structure could not be determined using Flack x parameter.

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