Direct *C*-nitration of cyclic α,β-unsaturated oximes under the action of sodium nitrite and acetic acid in methanol

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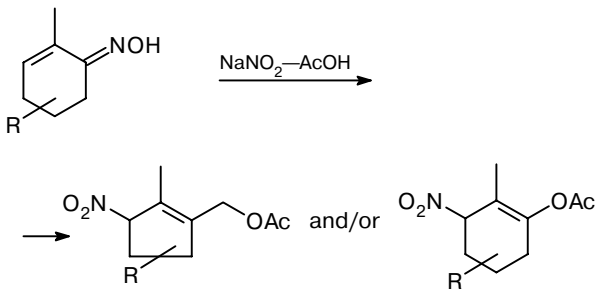
Using a number of cyclic α,β-unsaturated oximes of the terpene series and some simplest model compounds as examples, unsaturated oximes bearing a hydrogen atom at the β-carbon atom were demonstrated to be converted into β-hydroxyiminonitroalkenes under the action of sodium nitrite and acetic acid in methanol. In the case of the introduction of an alkyl substituent at the terminal carbon atom of the diene C=C—C=NOH fragment, the reaction performed under the same conditions gave rise exclusively to conjugated ketone (a deoximation product).

Key words: α,β-unsaturated oximes, conjugated ketones, nitrosation, *C*-nitration, deoximation, nitroalkenes, circular dichroism.

Recently, we have reported[1] that oximes of a number of cyclic α,β-unsaturated ketones were converted under the action of sodium nitrite in acetic acid into unsaturated nitroacetates (Scheme 1).

Scheme 1

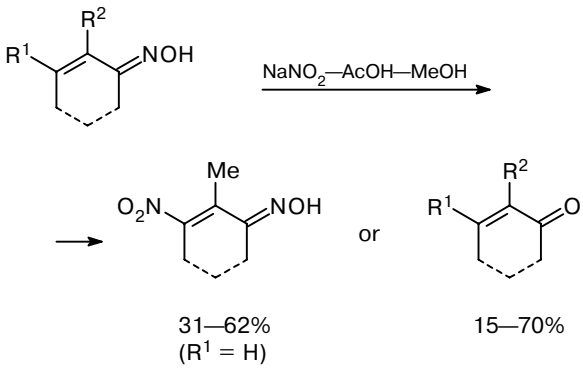


Reaction conditions: +5—10 °C, 2—4 h.

The use of methanol as the solvent with retention of the above-mentioned nitrosating system ($NaNO_2$—AcOH) was found to have a dramatic effect on the course of the reaction giving rise to different products, predominantly, β-hydroxyiminonitroalkenes (Scheme 2).

Since nitroalkenes are being extensively studied and are used as precursors in the synthesis of some heterocyclic compounds, natural compounds, and drugs,[2] we carried out detailed investigation of conversions of a number of α,β-unsaturated oximes of the terpene series and some structurally simpler model compounds under the action of the $NaNO_2$—AcOH system using methanol as the solvent. Below are presented the results of these investigations.

Scheme 2



R^1 = H, R^2 = Me; R^1 = Me, R^2 = H; R^1 = R^2 = Me

Reaction conditions: 4 h—7 days, ~20 °C.

Results and Discussion

We studied the behavior of oximes of (+)-car-2-en-4-one (**1**), (−)-carvone (**2**), 2-methylcyclohex-2-en-1-one (**3**), eucarvone (**4**), and pinocarvone (**5**) in the

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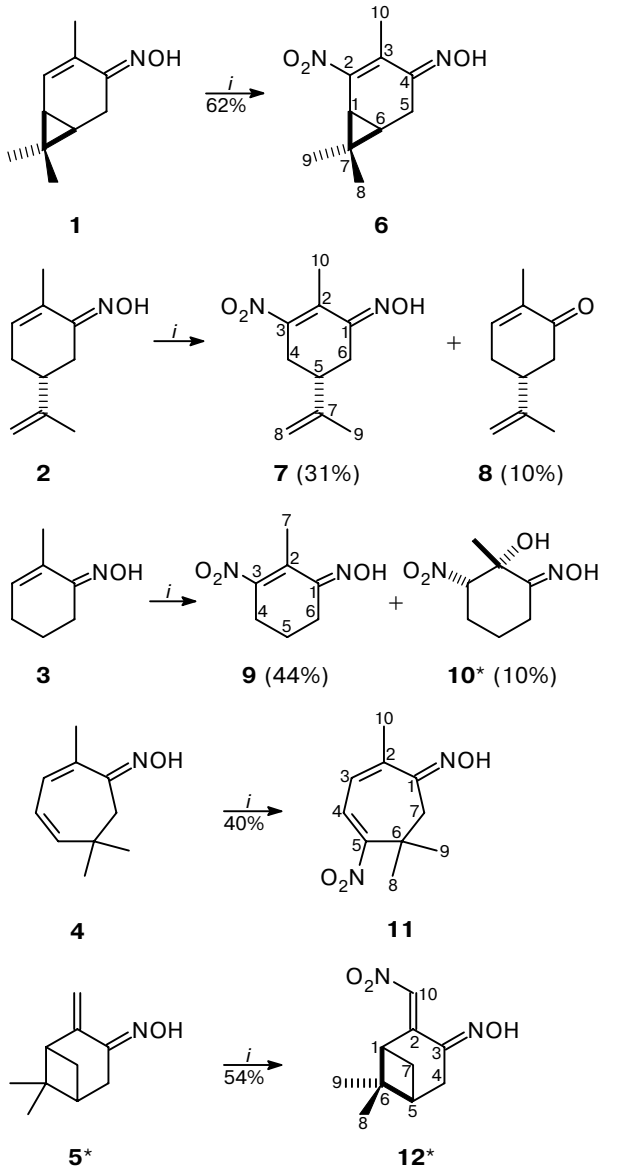
reactions with $NaNO_2$ and AcOH in MeOH (Scheme 3). The time required for complete conversion of the starting oximes varied from 4 h to 7 days and can be represented as the following sequence: $t_1 > t_3 > t_4 > t_2 \approx t_5$. In the case of oxime **1**, the degree of conversion was only 35% although more than 10 equiv. of $NaNO_2$ were used and the reaction was carried out for 7 days. The reaction of carvone oxime **2** afforded ketone of carvone (**8**) along with the major product. After chromatography, the yield of **8** was 10%.

Scheme 3



Reagents and conditions: *i*. $NaNO_2$—AcOH—MeOH, ~20 °C, 4 h—7 days.

In all cases, conjugated nitro oximes **6**, **7**, **9**, **11**, and **12** were obtained as the major reaction products (Scheme 3). Their structures were established by spectral methods. In the ^1H NMR spectra of the products, a signal for the olefinic proton at the β-carbon atom of the $\underline{H}C_\beta=C_\alpha-C=NOH$ fragment (in the case of the starting oximes **1**, **2**, **3**, and **5**) and a signal for the hydrogen atom at the terminal carbon atom of the triene $HC_\delta=C_\gamma-C_\beta=C_\alpha-C=NOH$ system (in the case of oxime **4**) disappear, while the remaining signals of the starting compounds (including the signal of $\underline{H}O-N=$) persist. Detailed analysis of the ^1H and ^{13}C NMR spectra suggested that the carbon skeleton of the initial oximes was retained in the reaction products. The mass spectra and the data from elemental analysis of the products are indicative of the introduction of the nitro group into the molecules. The IR spectra of the products have two intense absorption bands in the regions of 1325—1341 and 1509—1538 cm^{-1}, which are characteristic of the conjugated nitro group.

The formation of β-nitroalkenes from α,β-unsaturated oximes can occur through two essentially different pathways shown in Scheme 4.

First, the formation of nitroalkenes can be conceived as direct nitration, *i.e.*, as the replacement of the vinyl hydrogen atom at the β position with respect to the oxime group, the latter remaining intact (path *A*). This reaction pathway should afford products **6**, **7**, **9**, **11**, and **12**. Second, the reactions of oximes in the $NaNO_2$—AcOH system are generally considered as nitrosation because the product of addition of the nitrosonium cation NO^+ to the substrate is formed as the primary reaction product. The addition of NO^+ at the terminal atom of the diene system (at the β position with respect to the oxime group; path *B* in Scheme 4) should give rise to the nitroso group at the secondary carbon atom resulting in the appearance of the oxime group due to the subsequent obligatory tautomeric conversion. Taking into account that the $NaNO_2$—AcOH system, among other things, acts as an oxidizer and that the formation of nitro compounds upon oxidation of oximes is a well-known process, the conversion of the oxime group into the nitro group could be the final stage of the reaction according to path *B*.

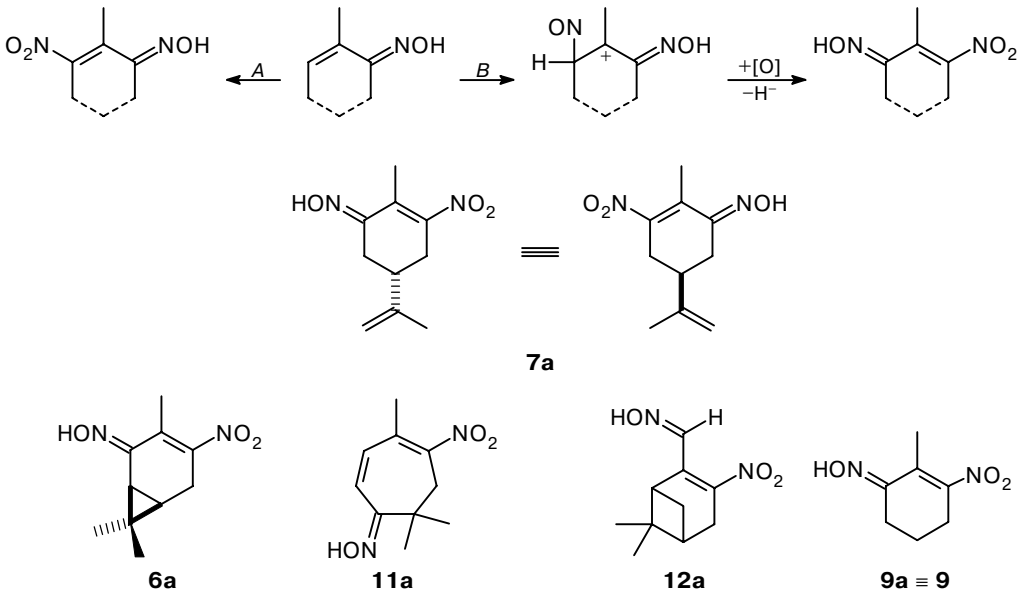
Hence, alternative structures **6a**, **7a**, **9a**,* **11a**, and **12a**, which could be formed due to conversion through path *B*, can be related to structures **6**, **7**, **9**, **11**, and **12**, respectively. Therefore, the unambiguous proof of structures **6**, **7**, **9**, **11**, and **12** will allow an understanding of the mechanism of formation of nitroalkenes from unsaturated oximes.

In all starting oximes **1—5**, the oxime group has the *E* configuration. A comparison of the chemical shifts of the signals for the atoms of the adjacent methylene group in the ^1H and ^{13}C NMR spectra of the initial oximes and the corresponding nitroolefins unambigu-

* Hereinafter, the racemate is marked with an asterisk (★).

* **9a** ≡ **9**.

Scheme 4



ously indicates that the oxime group in the nitration products retains the *E* configuration. In the ^{13}C NMR spectrum of nitroalkene **12** prepared from pinocarvone oxime (**5**), the signal at δ_C 149.68 corresponds to the azomethine C(3) atom, which has the vicinal spin-spin coupling constant with the hydrogen atom of the HO—N=C(3) oxime group ($^3J_{C(3)-H}$ = 8.1 Hz). In addition, the H(10) atom has the spin-spin coupling constants with the C(1) and C(3) atoms ($^3J_{H(10)-C(1)}$ = 6.5 Hz; $^3J_{H(10)-C(3)}$ = 4.3 Hz) whose values indicate that the H(10) atom is in the *cis* orientation with respect to the C(3) atom. The structure of nitro derivative **6** prepared from oxime **1** was proved analogously. In the 2D $^{13}C-^1H$ COSY NMR spectrum of product **6** at the long-range spin-spin coupling constants $^{2,3}J$ (tuning to J = 10 Hz), the only cross-peak at δ_C 152.44 (the signal for the azomethine C(4) atom) was observed for the signal of HO—N= (δ_H 11.89). This cross-peak, in turn, has cross-peaks with the H(5α) and H(5β) atoms at δ_H 2.64 and δ_H 2.75, respectively. These facts provide unambiguous support for structure **6** and allows one to reject alternative structure **6a**.

For nitro compounds **7** and **9**, the origin of the nitro group cannot be inferred from the NMR spectral data. Hence, we proved structure **7** based on the fact that the corresponding product was prepared from optically active carvone oxime (**2**).

It is known that the chiroptical properties of compounds are determined by their spatial molecular structures. For α,β-unsaturated ketones, there are simple correlations between the observed Cotton effect and the three-dimensional molecular structure.[3] However, no analogous regularities have been revealed for oximes of α,β-unsaturated ketones because of a small number of the models studied. It can only be said with assurance that the shape of the circular dichroism curves (CD curves) correlates with the *syn*/*anti* isomerism of the oxime group.[4–6]

Since the oxime group in all compounds under consideration has the *E* configuration, the shape of the CD curves should be determined only by the absolute configuration of these compounds. The CD curve of oxime **1** has two extrema with opposite signs of the Cotton effect, *viz.*, the negative effect at λ = 227 nm ($\Delta\varepsilon = -8.9$ mol^{-1} L cm^{-1}, π→π* transition) and the positive extremum at λ = 263 nm ($\Delta\varepsilon = +8.7$ mol^{-1} L cm^{-1}, n→π* transition) (Fig. 1). A comparison of the CD curves of oxime **1** and compound **6** clearly demonstrates that the extrema are shifted bathochromically (227 → 283 nm and 263 → 348 nm) on going from unsaturated oxime to nitro oxime due to conjugation of the diene system with the nitro group; in this case the signs of both extrema are retained and the intensity of dichroic absorption decreases. The Cotton effects in the CD curve of (−)-carvone oxime (**2**) are opposite in sign (λ = 222 nm with $\Delta\varepsilon = +4.1$ mol^{-1} L cm^{-1} and λ = 247 nm with $\Delta\varepsilon = -3.4$ mol^{-1} L cm^{-1}) to those observed in the CD curve of oxime **1**. On going from oxime **2** to nitro oxime **7**, only the bathochromic shift of the extrema is observed (222 → 275 nm and 247 → 341 nm) with retention of the signs of the Cotton effects. This is evidence for structure **7** because the signs of the Cotton effects in the case of structure **7a** would be expected to be reversed on going from oxime to nitro oxime.

A comparison of the ^1H and ^{13}C NMR spectra of eucarvone oxime (**4**) and nitroolefin **11** demonstrated that the chemical shifts of the C(7), H(7), C(10), and H(10) atoms located in the vicinity of the oxime group differ only slightly, which is indicative of retention of its

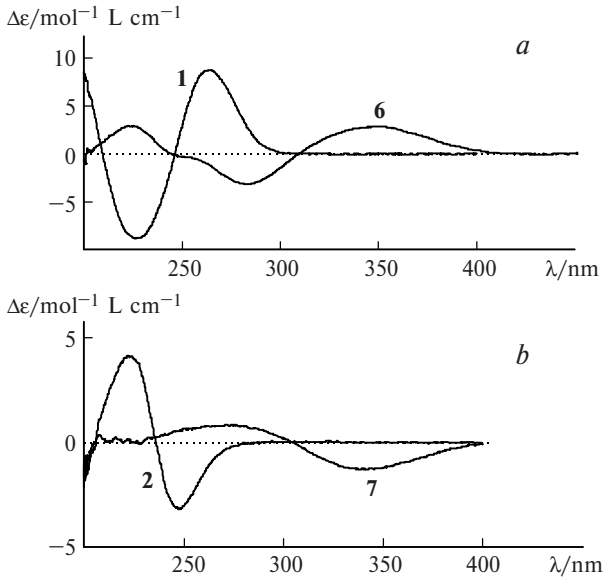


Fig. 1. Circular dichroism curves for oximes of α,β-unsaturated terpenic ketones **1** (*a*) and **2** (*b*) and the corresponding β-nitro derivatives of α,β-unsaturated ketoximes **6** (*a*) and **7** (*b*).

position in the molecule. Otherwise (for structure **11a**), substantial shifts of the signals for the C(7) and H(7) atoms, and, particularly, for the C(10) and H(10) atoms, would be observed.

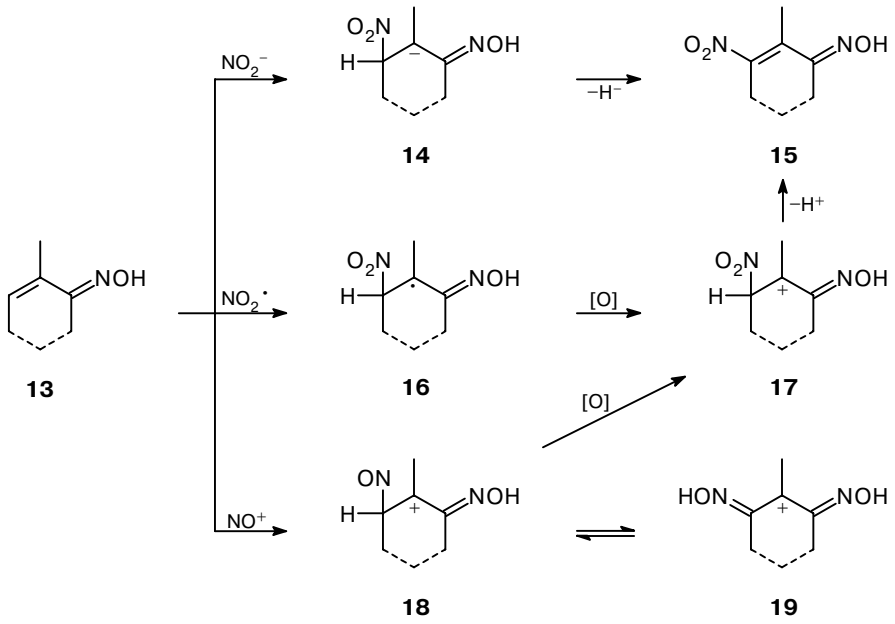
Hence, the terminal hydrogen atom of the conjugated $\underline{H}(C{=}C{-})_nC{=}NOH$ system (n = 1 or 2) in α,β-unsaturated cyclic oximes **1—5** is replaced by the nitro group under the action of $NaNO_2$ and AcOH in MeOH with retention of the C=NOH function of the starting oxime as exemplified by products **6**, **7**, **11**, and **12**.

Using structurally simple oximes of acyclic α,β-unsaturated ketones as examples, it has been shown many times[7—10] how the conditions of nitrosation (the change of the nitrosating agent, the performance of the reaction under an inert atmosphere or in the presence of atmospheric oxygen, the use of other co-oxidizers or transition metal salts) influence the qualitative and quantitative compositions of the conversion products. However, in no case did the change of the solvent result in the formation of the predominating product of the fundamentally different type starting from the same oxime. The reaction described in the present study is the first example of this kind. The change of the solvent (in essence, the use of MeOH as a diluent instead of a large excess of AcOH) gave rise to α,β-unsaturated β-nitro oximes rather than to unsaturated nitroacetates. The following facts were unexpected. First, the oxime group of the initial molecule is retained in the final product in spite of the facts that the reaction proceeds in the presence of a large excess of the nitrosating agent and that the reactions of oximes generally involve the attack of the nitrosating species occurring primarily on the C=N—OH group. Second, under the conditions of nitrosation, the trisubstituted double carbon—carbon bond undergoes nitration. In this case, the oxime group exerts an activating effect because the reactions does not take place in its absence (in the case of the corresponding olefinic hydrocarbons). The carbonyl group does not exhibit such an effect, which was exemplified by the reaction of carvone (**8**). Thus, ketone **8** did not react with an eightfold excess of the $NaNO_2$—AcOH mixture in MeOH during 5 days (TLC and ^1H NMR). In addition, it should be noted that examples of nitration of the C=C double bond under the action of sodium or potassium nitrites have been reported in the literature;[11—13] however, the latter reactions were carried out under conditions of electrochemical oxidation,[11] with the use of ultrasonic activation, or by heating with the addition of co-oxidizers, *viz.*, $Ce(NH_4)_2(NO_3)_6$[12] or iodine.[13] In the case of nitrosation of α,β-unsaturated oximes with $NaNO_2$ and AcOH, no additional oxidizers and ultrasonic activation are needed. The proposed procedure for the synthesis of conjugated nitro oximes is an alternative to the procedure, which has been developed previously[14] for the synthesis of a nor derivative of compound **9** based on oximation of the available nitroolefin under the action of $NaNO_2$ and alkyl nitrite in DMSO.

To account for the formation of nitro oximes in these reactions, mechanisms of two alternative types, *viz.*, radical and ionic, can be proposed (Scheme 5). In the case of the ionic mechanism, the nucleophilic addition accompanied by the primary attack of the nitrite anion at the terminal position of the conjugated system (**13** → **14**) should be, apparently, excluded from consideration because the nucleophilic addition of NO_2^- to the C=C double bond under the condition used is unlikely. According to the radical mechanism, the $NO_2^{\bullet}$ radical acts as a nitrating species, which can be generated from the nitrite anion.[15] This species attacks the C=C bond at the terminal position of the heterodiene system of the starting oxime **13**. Then radical intermediate **16** is oxidized to carbocation **17** under the action of the oxidizer (a nitrosating agent or atmospheric oxygen) followed by deprotonation to form the final product **15**. An analogous mechanism for nitration of alkenes has been proposed previously.[12] In the cited study, cerium ammonium nitrate was used as a co-oxidizer. It has been demonstrated that the reaction in the absence of the co-oxidizer proceeded much more slowly to give the final nitroolefin in lower yield.

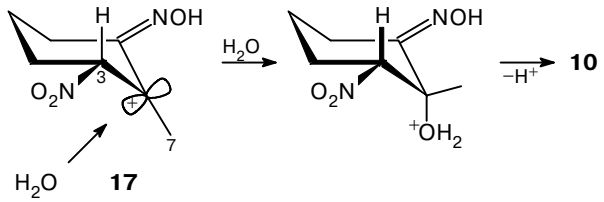
The addition of the electrophilic NO^+ species at the terminal carbon atom of the diene system (C(3)-nitrosation) followed by oxidation of cation **18** to nitro derivative **17** seems to be preferential. Within the framework of this scheme, it can be assumed that oxidation **18** → **17** proceeds much more rapidly than prototropic rearrangement **18** → **19**. Otherwise, the formation of symmetrical cation **19** would be expected, which, in the case of optically active starting compounds (for example, oxime **2**), would give rise to

Scheme 5



racemic nitro oxime. However, this is contradictory to the observed optical activity of compound **7**. The appearance of alcohol **10** among products of nitrosation[16] of oxime **3** is an argument in favor of the formation of intermediate cation **17**. Thus, the nucleophilic addition of a water molecule at the cationic center of intermediate **17** adopting the most stable conformation with the pseudoequatorial nitro group, which proceeds as the sterically most favorable antiparallel attack (Scheme 6), should afford alcohol with the *cis* arrangement of the nitro and hydroxy groups. This situation was proved based on the NMR spectral data.

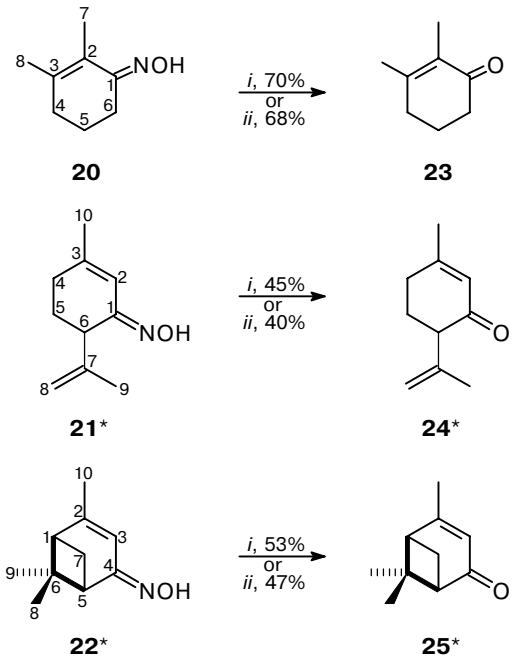
Scheme 6



Analysis of the spin-spin coupling constants $^3J_{H(3)-C(7)}$ and $^3J_{H(3)-H(4)}$ for the H(3) atom in the NMR spectra of compound **10** revealed the relative arrangement of the substituents in the molecule. The presence of the spin-spin coupling constant $^3J_{H(3)-H(4)}$ = 11.0 Hz is indicative of the axial position of the H(3) atom. In the case of the axial arrangement of the H(3) atom, the presence of the spin-spin coupling constant $^3J_{H(3)-C(7)}$ = 2.2 Hz points to the equatorial position of the methyl group (in the case of the axial arrangement of the methyl group, the spin-spin coupling constant $^3J_{H(3)-C(7)}$ should be equal to 6—8 Hz).

The conversion of oximes of α,β-unsaturated cyclic ketones into conjugated nitro oximes discovered by us is the reaction common to a series of structurally related unsaturated oximes bearing substituents at the α posi-

Scheme 7



Reagents and conditions: *i.* $NaNO_2$—AcOH—MeOH, ~20 °C, 4—6 h; *ii.* $NaNO_2$—AcOH, +5—10 °C, 1—3 h.

tion and at least one vinyl hydrogen atom at the β position. Nitrosation of cyclic oximes **20—22**, which do not contain the free β-vinyl hydrogen atom, with the $NaNO_2$—AcOH—MeOH system led to their oxidative deoximation[10,17—20] giving rise to the corresponding ketones **23—25** (Scheme 7). In the latter case, the reactions proceeded analogously to those in the $NaNO_2$—AcOH system, the yields of the reaction products being somewhat higher. The results obtained in the reactions involving oximes **20—22** is the first example of the conversion of α,β-unsaturated oximes under the conditions of nitrosation yielding ketone as the major conversion product. Previously, deoximation under the conditions of nitrosation has been observed only as a side process giving rise to carbonyl compounds as minor products.[9,10]

Experimental

The UV spectra were recorded on a Specord M-40 spectrophotometer in 95% EtOH ($c = 1 \cdot 10^{-4}$ mol L^{-1}). The IR spectra were measured on a Bruker Vector-22 instrument in KBr pellets (unless otherwise indicated) with the concentration of 0.25%. The mass spectra were obtained on a Finnigan MAT 8200 spectrometer (50—100 °C, EI, 70 eV). The ^1H and ^{13}C NMR spectra were recorded on Bruker AC-200 (200.13 MHz for ^1H and 50.32 MHz for ^{13}C) and Bruker AM-400 (400.13 MHz for ^1H and 100.61 MHz for ^{13}C) spectrometers for solutions with concentrations of 70—100 mg mL^{-1} at 25—27 °C. The signals of the solvent, *viz.*, chloroform-d ($\delta_C = 76.90$, $\delta_H = 7.24$) or dimethyl sulfoxide-d_6 ($\delta_C = 39.50$, $\delta_H = 2.50$), were used as the internal standard. The assignment of the signals was made using the ^{13}C NMR spectra recorded with the *J* modulation (proton-noise-decoupled spectra, the opposite phases for the signals of the atoms with the odd and even numbers of the attached protons, tuning to the constant $J = 135$ Hz) and based on the data of the 2D COSY spectra: (1) homonuclear ^1H—^1H correlation, (2) heteronuclear ^{13}C—^1H correlation at the direct spin-spin coupling constants ($J = 135$ Hz), and (3) heteronuclear ^{13}C—^1H correlation at the long-range spin-spin coupling constants ($J = 10$ Hz). Microanalyses were performed on Hewlett Packard 185 and Carlo Erba 1106 analyzers. The optical rotation was measured on a Polamat A polarimeter in $CHCl_3$. The circular dichroism spectra of compounds **1**, **2**, **6**, and **7** were recorded on a JASCO 600 spectropolarimeter (JASCO, Japan) in MeOH ($c = 10^{-4}$ mol L^{-1}) with the optical path of 1 cm.

The melting points were determined on a Kofler stage. Thin-layer chromatography was carried out on Silufol plates with a fixed SiO_2 layer. The spots were visualized by spraying with ethanolic solutions of vanilline (2 g of vanilline + 5 mL of concentrated H_2SO_4 in 150 mL of 95% EtOH) or iron(III) chloride (3 g of $FeCl_3 \cdot 6H_2O$ in 150 mL of 95% EtOH) followed by heating. Preparative column chromatography was carried out on KSK silica gel (particle size 0.140—0.315 mm) activated at 140 °C for 6—7 h.

(+)-3-Carene with $[\alpha]_{578}^{20}$ +16.0 (d_4^{20} 0.863) and α-pinene with $[\alpha]_{578}^{20}$ +20.4 (d_4^{20} 0.856) were prepared by rectification of turpentine obtained from Scotch pine (*Pinus silvestris*). To prepare oximes by nitrosochlorination—dehydrochlorination,[21] (+)-3-carene and α-pinene were converted into nitrosochlorides. Due to the low optical purity of α-pinene, the corresponding crystalline nitrosochloride was obtained as a racemate. (−)-Carvone (**8**) purchased from Fluka AG was used without additional purification.

Synthesis of the starting oximes. (+)-(1*S*,6*R*)-Car-2-en-4-one (*E*)-oxime (1) was prepared from (+)-3-carene according to a known procedure[21]: m.p. 93—94 °C (from EtOAc); *cf.* lit. data[22]: 94—95 °C; $[\alpha]_{578}^{24}$ +265 (*c* 2.37); *cf.* lit. data[22]: $[\alpha]_D$ +374 (EtOH). The ^1H and ^{13}C NMR spectra were reported in Ref. 23.

(−)-(4*R*)-*p*-Mentha-1(6),8-dien-2-one (*E*)-oxime (2) ((−)-carvone oxime) was prepared from (−)-carvone (**8**) according to a procedure reported previously[24]: m.p. 72—74 °C (from MeCN); *cf.* lit. data[25]: 72 °C; $[\alpha]_{578}^{19}$ −48 (*c* 4.89). ^{13}C NMR ($CDCl_3$), δ: 17.65 (q, C(10)); 20.67 (q, C(9)); 27.22 (t, C(6)); 30.25 (t, C(4)); 40.12 (d, C(5)); 110.05 (t, C(8)); 130.12 (d, C(3)); 132.63 (s, C(2)); 147.41 (s, C(7)); 156.14 (s, C(1)).

2-Methylcyclohex-2-en-1-one (*E*)-oxime (3) was prepared from 1-methylcyclohexene according to a known procedure[21]: m.p. 63—64 °C (from MeCN); *cf.* lit. data[21]: 63—64 °C. ^1H NMR ($CDCl_3$—CCl_4), δ: 1.73 (tt, 2 H, $H_2C(5)$, $J_1 = J_2 = 6.5$ Hz); 1.81 (dt, 3 H, C(2)Me, $J_1 = J_2 = 1.5$ Hz); 2.15 (m, 2 H, $H_2C(4)$); 2.58 (t, 2 H, $H_2C(6)$, $J = 6.5$ Hz); 5.97 (tq, 1 H, H(3), $J_1 = 5.0$ Hz, $J_2 = 1.5$ Hz); 9.20 (br.s, 1 H, HON=). ^{13}C NMR ($CDCl_3$—CCl_4), δ: 18.11 (q, C(7)); 21.37 (t, C(5)); 22.51 (t, C(6)); 25.25 (t, C(4)); 130.80 (s, C(2)); 132.80 (d, C(3)); 155.68 (s, C(1)).

2,6,6-Trimethylcyclohepta-2,4-dien-1-one (*E*)-oxime (4) (eucarvone oxime) was prepared from eucarvone[26] according to a known procedure[24]: m.p. 105—107 °C (from MeCN); *cf.* lit. data[27]: 105—106.5 °C. ^1H NMR ($CDCl_3$), δ: 1.11 (both s, 3 H each, $H_3C(8)$, $H_3C(9)$); 2.01 (s, 3 H, C(2)Me); 2.77 (s, 2 H, $H_2C(7)$); 5.57 (dd, 1 H, H(4), $J_1 = 11.5$ Hz, $J_2 = 6.5$ Hz); 5.60 (d, 1 H, H(5), $J = 11.5$ Hz); 5.91 (d, 1 H, H(3), $J = 6.5$ Hz); 10.20 (br.s, 1 H, HO—N=). ^{13}C NMR ($CDCl_3$), δ: 21.87 (q, C(10)); 27.90 (q, C(8), C(9)); 35.07 (s, C(6)); 35.65 (t, C(7)); 121.50 (d, C(4)); 127.37 (d, C(5)); 135.37 (s, C(2)); 144.66 (d, C(3)); 157.67 (s, C(1)).

(±)-6,6-Dimethyl-2-methylenebicyclo[3.1.1]heptan-3-one (*E*)-oxime (5) (pinocarvone oxime) was prepared from α-pinene according to a known procedure[21]: m.p. 131—133 °C (from light petroleum); *cf.* lit. data[21]: 132—134 °C (from hexane). The ^1H and ^{13}C NMR spectra were reported in Ref. 23.

2,3-Dimethylcyclohex-2-en-1-one (*E*)-oxime (20) was prepared from ketone **23** [26] according to a known procedure[24]: m.p. 102—104 °C (from MeCN). UV (EtOH), λ_{max}/nm (ε): 204 (8500), 238 (31500). IR (film), ν/cm^{-1}: 760, 819, 860, 904, 925 (=N—OH); 1428, 1611 (C=N); 1630 (C=C). IR ($CHCl_3$), ν/cm^{-1}: 3275 and 3587 (OH). ^1H NMR ($CDCl_3$—CCl_4), δ: 1.69 (tt, 2 H, H(5), $J_1 = J_2 = 6.5$ Hz); 1.79 (br.s, 3 H, C(3)Me); 1.82 (s, 3 H, C(2)Me); 2.12 (br.t, 2 H, $H_2C(4)$, $J = 6.5$ Hz); 2.56 (t, 2 H, $H_2C(6)$, $J = 6.5$ Hz); 9.37 (br.s, 1 H, =NOH, $W_{1/2} = 10$ Hz). ^{13}C NMR ($CDCl_3$—CCl_4), δ: 12.40 (q, C(7)); 20.72 (q, C(8)); 20.94 (t, C(5)); 22.35 (t, C(6)); 32.14 (t, C(4)); 124.36 (s, C(2)); 139.63 (s, C(3)); 157.08 (s, C(1)). MS, *m/z* (I_{rel} (%)): 139 $[M]^+$ (100), 122 (57), 106 (19), 95 (25), 94 (15), 93 (37), 81 (36), 80 (16), 79 (34), 77 (18), 67 (23), 55 (15), 53 (20), 41 (31), 39 (20). Found (%): C, 68.9; H, 9.5; N, 10.1. $C_8H_{13}NO$. Calculated (%): C, 69.03; H, 9.41; N, 10.06.

(±)-*p*-Mentha-1,8-dien-3-one (*E*)-oxime (21) (isopiperitenone oxime) was prepared from **24**[28] according to a procedure reported previously[24]: m.p. 141—143 °C (from MeCN). UV (EtOH), λ_{max}/nm (ε): 205 (7000), 242 (19000). IR (film), ν/cm^{-1}: 771, 875, 900 (=CH_2); 937 (N—O); 1150, 1220, 1245, 1375, 1430, 1644 (C=C); 3087 (=C—H). IR ($CHCl_3$), ν/cm^{-1}: 3275 and 3600 (OH). ^1H NMR ($CDCl_3$—CCl_4), δ: 1.40 (s, 3 H,

C(7)Me); 1.70—2.05 (m, 2 H, H(5a), H(5b)); 1.90 (dd, 3 H, C(3)Me, $J_1 = J_2 = 1.5$ Hz); 2.12 (br.t, 2 H, H(4a), H(4b), $J = 5.8$ Hz); 3.02 (dd, 1 H, H(6), $J_1 = 8.2$ Hz, $J_2 = 4.5$ Hz); 4.73 (s, 2 H, H(8a), H(8b)); 6.61 (q, 1 H, H(2), $J = 1.5$ Hz); 9.72 (br.s, 1 H, HON=). ^{13}C NMR ($CDCl_3$—CCl_4)*, δ: 20.01 (q, C(9)); 24.01 (q, C(10)); 26.79*** (t, C(5)); 29.53*** (t, C(4)); 45.19 (d, C(6)); 112.82 (t, C(8)); 113.07 (d, C(2)); 144.45 (s, C(7)); 148.80 (s, C(3)); 153.90 (s, C(1)). MS, m/z (I_{rel} (%)): 165 $[M]^+$ (99), 164 (62), 151 (100), 150 (14), 149 (84), 147 (25), 136 (46), 133 (35), 132 (38), 131 (22), 119 (15), 118 (18), 117 (16), 108 (26), 107 (23), 106 (22), 105 (20), 94 (20), 93 (22), 91 (38), 81 (21), 80 (16), 79 (35), 77 (27), 68 (14), 67 (25), 65 (17), 55 (19). Found (%): C, 72.9; H, 9.1; N, 8.6. $C_{10}H_{15}NO$. Calculated (%): C, 72.69; H, 9.15; N, 8.48.

(±)-2,6,6-Trimethylbicyclo[3.1.1]hept-2-en-4-one (22) oxime (verbenone oxime) was prepared from racemic verbenone (**25**)[24] synthesized from α-pinene as a mixture of the *E* and *Z* isomers in a ratio of 3 : 2, m.p. 121—123 °C (from MeCN); *cf.* lit. data[29]: 119—120 °C (from naphtha).

***E* isomer.** ^{1}H NMR ($CDCl_3$—CCl_4), δ: 1.02 (s, 3 H, $H_3C(8)$); 1.40 (s, 3 H, $H_3C(9)$); 1.68 (d, 1 H, H(7α), $J = 8.2$ Hz); 1.90 (dd, 3 H, C(2)Me, $J_1 = J_2 = 1.5$ Hz); 2.21 (m, 1 H, H(1)); 2.70 (m, 2 H, H(5), H(7β)); 6.44 (dq, 1 H, H(3), $J_1 = J_2 = 1.5$ Hz); 9.72 (br.s, 1 H, HON=). ^{13}C NMR ($CDCl_3$—CCl_4), δ: 21.95 (q, C(8)); 23.55 (q, C(10)); 26.24 (q, C(9)); 37.32 (t, C(7)); 47.81 (s, C(6)); 48.13 (d, C(5)); 49.35 (d, C(1)); 110.23 (d, C(3)); 157.01 (s, C(2)); 158.60 (s, C(4)).

***Z* isomer.** ^{1}H NMR ($CDCl_3$—CCl_4), δ: 0.99 (s, 3 H, $H_3C(8)$); 1.43 (s, 3 H, $H_3C(9)$); 1.58 (d, 1 H, H(7α), $J = 8.7$ Hz); 1.85 (dd, 3 H, C(2)Me, $J_1 = J_2 = 1.5$ Hz); 2.20 (m, 1 H, H(1)); 2.56 (m, 1 H, H(7β)); 3.60 (ddd, 1 H, H(5), $J_1 = J_2 = 5.5$ Hz, $J_3 = 1.5$ Hz); 5.78 (dq, 1 H, H(3), $J_1 = J_2 = 1.5$ Hz); 9.72 (br.s, 1 H, HON=). ^{13}C NMR ($CDCl_3$—CCl_4), δ: 22.32 (q, C(8)); 23.05 (q, C(10)); 26.18 (q, C(9)); 36.03 (t, C(7)); 41.46 (d, C(5)); 47.01 (s, C(6)); 49.17 (d, C(1)); 116.11 (d, C(3)); 152.89 (s, C(2)); 160.94 (s, C(4)).

Nitration of α,β-unsaturated oximes in methanol (general procedure *A*). Powdered $NaNO_2$ was added portionwise with stirring to a solution of oxime in a mixture of MeOH and AcOH at ~20 °C. After the starting compound was consumed (TLC control), the mixture was diluted with water (2—3-fold by volume) and an excess of AcOH was neutralized with a 25% aqueous solution of NH_3 to pH 9—10 and extracted three times with CH_2Cl_2. The combined organic extracts were washed successively with water and a saturated aqueous solution of NaCl and dried with anhydrous $MgSO_4$. The solvent was removed *in vacuo* and the residue was chromatographed on SiO_2 (gradient elution with the Et_2O—light petroleum system).

Deoximation of α,β-unsaturated oximes in acetic acid (general procedure *B*). Powdered $NaNO_2$ was added portionwise with stirring to a solution of oxime in glacial AcOH at +5—10 °C. After the starting compound was consumed (TLC control), the mixture was diluted with water and extracted with Et_2O. The combined organic extracts were washed successively with a 0.5 *M* aqueous solution of Na_2CO_3 and a saturated aqueous solution of NaCl and dried with anhydrous $MgSO_4$. The solvent was removed *in vacuo* and the residue was chromatographed on SiO_2 (gradient elution with the Et_2O—light petroleum system).

The reaction of carvone (**8**) (0.50 g, 3.3 mmol) with $NaNO_2$ (1.88 g, 27.2 mmol) and AcOH (3 mL) in MeOH (10 mL) was carried out according to procedure *A* for 3 days. After standard treatment and removal of the solvent, a pale-yellow oil with a characteristic carvone odor was obtained in a yield of 0.46 g. The ^{1}H and ^{13}C NMR and IR spectral data are identical with the corresponding characteristics of the starting ketone.

(+)-1*S*,6*R*-2-Nitrocar-2-en-4-one (*E*)-oxime (6). The reaction of oxime **1** (400 mg, 2.4 mmol) with $NaNO_2$ (2.00 g, 29.0 mmol) and AcOH (2 mL) in MeOH (50 mL) was carried out according to procedure *A* for 7 days. Chromatography afforded product **6** (112 mg, 62% with respect to the consumed oxime) and the starting compound **1** (259 mg). M.p. of compound **6** was 131—133 °C (from a hexane—EtOAc mixture). $[\alpha]_{578}^{16}$ +364 (*c* 2.44). UV (EtOH), λ_{max}/nm (ε): 211 (7900), 236 (9500), 323 (3600). IR (KBr), ν/cm^{-1}: 784, 970 (=N—OH); 990, 1417, 1338 and 1538 (NO_2); 1616 (C=C). IR ($CHCl_3$), ν/cm^{-1}: 3280 and 3568 (OH). ^{1}H NMR (DMSO-d_6), δ: 0.80 (s, 3 H, $H_3C(8)$); 1.17 (s, 3 H, $H_3C(9)$); 1.40 (dd, 1 H, H(6), $J_1 = 8.8$ Hz, $J_2 = 8.4$ Hz); 1.74 (d, 1 H, H(1), $J = 8.8$ Hz); 2.00 (s, 3 H, $H_3C(10)$); 2.64 (dd, 1 H, H(5β), $J_1 = 20.0$ Hz, $J_2 = 8.4$ Hz); 2.75 (d, 1 H, H(5α), $J = 20.0$ Hz); 11.89 (s, 1 H, HO—N=). ^{13}C NMR (DMSO-d_6), δ: 12.05 (q, C(10)); 13.36 (q, C(8)); 17.54 (t, C(5)); 20.53 (d, C(6)); 23.68 (d, C(1)), 23.95 (s, C(7)); 26.24 (q, C(9)); 127.36 (s, C(3)); 148.96 (s, C(4)); 152.44 (s, C(2)). MS, m/z (I_{rel} (%)): 210 $[M]^+$ (29), 168 (100), 151 (27), 121 (17), 120 (17), 106 (19), 105 (18), 104 (18), 93 (24), 92 (19), 91 (29), 79 (21), 78 (21), 77 (37), 65 (19), 53 (19), 43 (19), 41 (50), 39 (22). Found (%): C, 57.3; H, 6.9; N, 13.4. $C_{10}H_{14}N_2O_3$. Calculated (%): C, 57.13; H, 6.71; N, 13.32.

(−)-(4*R*)-*p*-Mentha-6-nitro-1(6),8-dien-2-one (*E*)-oxime (7). The reaction of oxime **2** (0.66 g, 4.0 mmol) with $NaNO_2$ (1.10 g, 16.0 mmol) and AcOH (1.5 mL) in MeOH (10 mL) was carried out according to procedure *A* for 4 h (according to the ^{1}H NMR spectral data, the ratio **7** : **8** in the crude product was 2 : 1). After chromatography, product **7** (0.26 g, 31%) and carvone (**8**) (60 mg, 10%) were isolated. M.p. 120—122 °C (from a toluene—hexane mixture). $[\alpha]_{578}^{21}$ −214 (*c* 3.75). UV (EtOH), λ_{max}/nm (ε): 206 (6800), 228 (9800), 303 (4900). IR ($CHCl_3$), ν/cm^{-1}: 900 (=CH_2); 965 (N—O); 1341 and 1510 (NO_2); 1438, 1646 (C=C); 3093 (=CH_2); 3300 and 3575 (OH). ^{1}H NMR ($CDCl_3$—CCl_4), δ: 1.79 (dd, 3 H, C(7)Me, $J_1 = 1.2$ Hz, $J_2 = 0.8$ Hz); 2.05 (dd, 3 H, C(2)Me, $J_1 = 2.2$ Hz, $J_2 = 1.2$ Hz); 2.16 (dd, 1 H, H(6a), $J_1 = 16.7$ Hz, $J_2 = 11.7$ Hz); 2.48 (m, 1 H, H(5)); 2.68 (dq, 1 H, H(4a), $J_1 = 10.2$ Hz, $J_2 = 2.2$ Hz); 2.82 (ddd, 1 H, H(4b), $J_1 = 16.7$ Hz, $J_2 = 4.8$ Hz, $J_3 = 1.2$ Hz); 3.20 (ddd, 1 H, H(6b), $J_1 = 16.7$ Hz, $J_2 = 3.7$ Hz, $J_3 = 1.5$ Hz); 4.82 (dq, 1 H, H(8a), $J_1 = J_2 = 0.8$ Hz); 4.87 (dq, 1 H, H(8b), $J_1 = 1.2$ Hz, $J_2 = 0.8$ Hz); 9.11 (br.s, 1 H, HO—N=). ^{13}C NMR ($CDCl_3$—CCl_4), δ: 12.47 (q, C(10)); 20.64 (q, C(9)); 26.75 (t, C(6)); 31.65 (t, C(4)); 38.74 (d, C(5)); 111.56 (t, C(8)); 129.80 (s, C(2)); 145.27 (s, C(7)); 151.11 (s, C(1)), 155.48 (s, C(3)). MS, m/z (I_{rel} (%)): 146 (32), 132 (33), 131 (21), 130 (20), 120 (25), 118 (26), 106 (24), 105 (25), 93 (25), 91 (53), 79 (40), 78 (24), 77 (53), 67 (37), 65 (35), 53 (100), 52 (27), 51 (33), 43 (34), 41 (68). Found (%): C, 57.2; H, 6.6; N, 13.2. $C_{10}H_{14}N_2O_3$. Calculated (%): C, 57.13; H, 6.71; N, 13.32.

2-Methyl-3-nitrocyclohex-2-en-1-one (*E*)-oxime (9). The reaction of oxime **3** (5.40 g, 43.1 mmol) with $NaNO_2$ (11.90 g, 172.4 mmol) and AcOH (15 mL) in MeOH (100 mL) was carried out according to procedure *A* for 24 h. After standard treatment and removal of the solvent, a residue was obtained in a yield of 6.31 g. The residue was crystallized from a hexane—EtOAc mixture to obtain nitro oxime **9** (2.13 g). The mother liquor was chromatographed and an additional amount of product **9** (1.21 g, the total yield was 44%) along with hydroxynitro-substituted oxime **10** (1.42 g, 10%) were ob-

* Hereinafter, the assignments marked with asterisks (***) may be reverse.

tained. M.p. 138—138.5 °C (from an EtOAc—hexane mixture, sublimation at 90 °C). UV (EtOH), λ_{max}/nm (ε): 207 (4700), 226 (7800), 301 (3900). IR (KBr), ν/cm^{-1}: 771, 875, 978 (N—O), 1017, 1325, and 1513 (NO_2); 1618 (C=N); 1698 (C=C). IR ($CHCl_3$), ν/cm^{-1}: 3300 and 3575 (OH). ^{1}H NMR, ($CDCl_3$—CCl_4), δ: 1.87 (tt, 2 H, $H_2C(5)$, $J_1 = J_2 = 6.5$ Hz); 2.05 (t, 3 H, C(2)Me, $J = 2.0$ Hz); 2.64 (d, 2 H, $H_2C(6)$, $J = 6.5$ Hz); 2.70 (dq, 2 H, $H_2C(4)$, $J_1 = 6.5$ Hz, $J_2 = 2.0$ Hz); 8.85 (s, 1 H, HO—N=). ^{13}C NMR ($CDCl_3$—CCl_4), δ: 12.50 (q, C(7)); 19.88 (t, C(5)); 21.67 (t, C(6)); 26.78 (t, C(4)); 130.35 (s, C(2)); 151.64 (s, C(1)); 155.60 (s, C(3)). MS, *m/z* (I_{rel} (%)): 170 $[M]^+$ (76), 153 (100), 106 (22), 95 (62), 94 (29), 80 (32), 79 (49), 78 (23), 77 (67), 68 (24), 67 (49), 66 (21), 65 (34), 55 (24), 54 (44), 53 (57), 52 (28), 51 (31), 43 (49), 42 (21), 41 (81), 39 (58). Found (%): C, 49.5; H, 6.2; N, 16.5. $C_7H_{10}N_2O_3$. Calculated (%): C, 49.41; H, 5.92; N, 16.46.

(±)-*cis*-2-Hydroxy-2-methyl-3-nitrocyclohexan-1-one (*E*)-oxime (10), m.p. 99—102 °C (from MeCN). IR (KBr), ν/cm^{-1}: 704, 739, 848, 902, 946 (N—O); 1369 and 1555 (NO_2); 1380, 1429, 1440, 1664 (C=C). IR ($CHCl_3$), ν/cm^{-1}: 3562 and 3666 (OH). ^{1}H NMR (DMSO-d_6), δ: 1.31 (ddddd, 1 H, $H_{ax}(5)$, $J_1 = J_2 = J_3 = 12.0$ Hz, $J_4 = J_5 = 4.0$ Hz); 1.36 (s, 3 H, C(2)Me); 1.79 (ddd, 1 H, $H_{eq}(5)$, $J_1 = 12.0$ Hz, $J_2 = 5.0$ Hz, $J_3 = 4.0$ Hz); 1.84 (dddd, 1 H, $H_{eq}(4)$, $J_1 = 12.0$ Hz, $J_2 = J_3 = J_4 = 4.0$ Hz); 1.95 (ddd, 1 H, $H_{pseudo\text{-}ax}(6)$, $J_1 = 14.0$ Hz, $J_2 = 12.0$ Hz, $J_3 = 5.0$ Hz); 2.38 (dddd, 1 H, $H_{ax}(4)$, $J_1 = J_2 = 12.0$ Hz, $J_3 = 11.0$ Hz, $J_4 = 4.0$ Hz); 2.91 (ddd, 1 H, $H_{pseudo\text{-}eq}(6)$, $J_1 = 14.0$ Hz, $J_2 = J_3 = 4.0$ Hz); 4.54 (dd, 1 H, H(3), $J_1 = 11.0$ Hz, $J_2 = 4.0$ Hz); 5.47 (s, 1 H, HO); 10.87 (s, 1 H, HO—N=). ^{13}C NMR (DMSO-d_6), δ: 17.41 (t, C(5)); 18.63*** (t, C(4)); 20.79 (q, C(7)); 23.16*** (t, C(6)); 69.93 (s, C(2)); 90.08 (d, C(3)); 156.07 (s, C(1)). MS, *m/z* (I_{rel} (%)): 170 $[M^+ - H_2O]$ (7), 125 (9), 124 (55), 99 (8), 98 (13), 83 (17), 82 (24), 79 (9), 71 (9), 55 (26), 54 (12), 53 (9), 43 (100), 41 (17). Found (%): C, 44.8; H, 6.5; N, 14.9. $C_7H_{12}N_2O_4$. Calculated (%): C, 44.68; H, 6.43; N, 14.89.

2,6,6-Trimethyl-5-nitrocyclohepta-2,4-dien-1-one (*E*)-oxime (11). The reaction of oxime **4** (0.50 g, 3.0 mmol) with $NaNO_2$ (1.25 g, 18.1 mmol) and AcOH (3 mL) in MeOH (15 mL) was carried out according to procedure *A* for 6 h. After chromatography, product **11** was isolated in a yield of 253 mg (40%), m.p. 148—150 °C (from CCl_4). UV (EtOH), λ_{max}/nm (ε): 211 (8800), 265 (5200), 294 (6900), 365 (6700). IR ($CHCl_3$), ν/cm^{-1}: 962 and 971 (=N—OH); 1457, 1335, and 1515 (NO_2); 1588 (C=C); 3282 and 3592 (OH). ^{1}H NMR, ($CDCl_3$—CCl_4), δ: 1.35 (both s, 3 H each, $H_3C(8)$, $H_3C(9)$); 2.09 (d, 3 H, C(2)Me, $J = 1.3$ Hz); 2.90 (s, 2 H, $H_2C(7)$); 5.99 (dq, 1 H, H(3), $J_1 = 9.0$ Hz, $J_2 = 1.3$ Hz); 6.63 (d, 1 H, H(4), $J = 9.0$ Hz); 9.42 (br.s, 1 H, HO—N=). ^{13}C NMR ($CDCl_3$—CCl_4), δ: 21.44 (q, C(10)); 25.36 (q, C(8), C(9)); 36.29 (t, C(7)); 37.33 (s, C(6)); 122.51 (d, C(3)); 123.28 (d, C(4)); 144.13 (s, C(2)); 156.47 (s, C(5)); 161.10 (s, C(1)). MS, *m/z* (I_{rel} (%)): 210 $[M]^+$ (98), 164 (100), 146 (30), 132 (66), 131 (68), 130 (30), 120 (26), 117 (30), 106 (30), 105 (30), 104 (29), 103 (33), 91 (57), 79 (30), 78 (26), 77 (60), 67 (25), 65 (40), 53 (49), 51 (33), 45 (34), 43 (45), 41 (66), 39 (66). Found (%): C, 57.3; H, 6.7; N, 13.3. $C_{10}H_{14}N_2O_3$. Calculated (%): C, 57.13; H, 6.71; N, 13.32.

(±)-6,6-Dimethyl-2-methylene-(10*E*)-nitrobicyclo[3.1.1]heptan-3-one (*E*)-oxime (12) ((10*E*)-nitropinocarvone oxime). The reaction of oxime **5** (500 mg, 3.02 mmol) with $NaNO_2$ (1.04 g, 15.1 mmol) and AcOH (1.7 mL) in MeOH (15 mL) was carried out according to procedure *A* for 4.5 h. After chromatography, nitro oxime **12** was isolated as a yellow viscous oil (343 mg, 1.63 mmol, 54%), which crystallized upon storage. M.p. 69—71 °C (from a hexane—toluene mixture). UV (EtOH), λ_{max}/nm (ε): 208 (5400), 231 (6700), 312 (7200). IR ($CHCl_3$), ν/cm^{-1}: 968 (=N—OH); 1341 and 1509 (NO_2); 1645 (C=C); 3112 (=CH); 3288 and 3577 (OH). ^{1}H NMR ($CDCl_3$), δ: 0.82 (s, 3 H, $H_3C(8)$); 1.21 (d, 1 H, H(7α), $J = 11.0$ Hz); 1.39 (s, 3 H, $H_3C(9)$); 2.18 (dddd, 1 H, H(5), $J_1 = J_2 = 5.5$ Hz, $J_3 = 3.5$ Hz, $J_4 = 2.5$ Hz); 2.60 (dddd, 1 H, H(7β), $J_1 = 11.0$ Hz, $J_2 = J_3 = 5.5$ Hz, $J_4 = 2.5$ Hz); 2.72 (ddd, 1 H, H(4α), $J_1 = 19.0$ Hz, $J_2 = J_3 = 2.5$ Hz); 2.91 (dd, 1 H, H(4β), $J_1 = 19.0$ Hz, $J_2 = 3.5$ Hz); 3.99 (dd, 1 H, H(1), $J_1 = J_2 = 5.5$ Hz); 7.69 (s, 1 H, H(10)); 9.20 (br.s, 1 H, HON=). ^{13}C NMR (DMSO-d_6), δ: 21.13 (q, C(8)); 26.08 (q, C(9)); 29.11*** (t, C(4)); 29.22*** (t, C(7)); 36.92 (d, C(5)); 41.36 (s, C(6)); 43.16 (d, C(1), $^3J_{C(1)-H(10)} = 6.5$ Hz); 130.49 (d, C(10), $^3J_{C(10)-H(1)} = 3.1$ Hz); 149.67 (s, C(3), $^3J_{C(3)-HON} = 8.1$ Hz, $^3J_{C(3)-H(10)} = 4.3$ Hz); 150.32 (s, C(2), $^2J_{C(2)-H(10)} = 2.4$). MS, *m/z* (I_{rel} (%)): 167 (18), 152 (21), 148 (17), 146 (28), 136 (28), 134 (20), 132 (35), 131 (18), 122 (32), 121 (19), 120 (65), 119 (17), 106 (21), 105 (26), 104 (17), 94 (21), 93 (41), 92 (41), 91 (36), 81 (16), 80 (20), 79 (31), 78 (22), 77 (50), 69 (38), 68 (17), 67 (34), 66 (18), 65 (37), 55 (24), 53 (33), 52 (21), 51 (23), 43 (66), 41 (100), 39 (51). Found (%): C, 56.9; H, 6.7; N, 13.2. $C_{10}H_{14}N_2O_3$. Calculated (%): C, 57.13; H, 6.71; N, 13.32.

2,3-Dimethylcyclohex-2-en-1-one (23). The reaction of oxime **20** (120 mg, 0.86 mmol) with $NaNO_2$ (238 mg, 3.44 mmol) and AcOH (0.5 mL) in MeOH (5 mL) was carried out according to procedure *A* for 5 h. After chromatography, ketone **23** was isolated as a pale-yellow oil (75 mg, 0.60 mmol, 70%). The ^{1}H NMR spectrum is identical with that of ketone **23** used for the synthesis of oxime **20**.

The reaction of oxime **20** (120 mg, 0.86 mmol) with $NaNO_2$ (180 mg, 2.60 mmol) in AcOH (2 mL) was carried out according to procedure *B* for 2 h. After chromatography, ketone **23** was isolated as a pale-yellow oil (73 mg, 0.58 mmol, 68%).

(±)-*p*-Mentha-1,8-dien-3-one (24) (isopiperitenone). The reaction of oxime **21** (190 mg, 1.15 mmol) with $NaNO_2$ (318 mg, 4.60 mmol) and AcOH (0.5 mL) in MeOH (5 mL) was carried out according to procedure *A* for 6 h. After chromatography, ketone **24** was isolated as a pale-yellow oil (78 mg, 0.52 mmol, 45%).

The reaction of oxime **21** (190 mg, 1.15 mmol) with $NaNO_2$ (164 mg, 2.37 mmol) in AcOH (3 mL) was carried out according to procedure *B* for 3 h. After chromatography, ketone **24** was isolated as a pale-yellow oil (69 mg, 0.46 mmol, 40%). ^{1}H NMR ($CDCl_3$), δ: 1.70 (br.s, 3 H, C(7)Me); 1.92 (ddd, 3 H, C(3)Me, $J_1 = 1.5$ Hz, $J_2 = 1.0$ Hz, $J_3 = 0.9$ Hz); 1.95—2.20 (m, 2 H, H(5α), H(5β)); 2.29 (m, 2 H, H(4α), H(4β)); 2.88 (ddd, 1 H, H(6), $J_1 = 10.0$ Hz, $J_2 = 5.3$ Hz, $J_3 = 0.9$ Hz); 4.69 (ddq, 1 H, H(8a), $J_1 = 1.5$ Hz, $J_2 = 1.0$ Hz, $J_3 = 0.9$ Hz); 4.88 (dq, 1 H, H(8b), $J_1 = J_2 = 1.5$ Hz); 5.82 (ddq, 1 H, H(2), $J_1 = J_2 = J_3 = 1.5$ Hz). ^{13}C NMR ($CDCl_3$), δ: 20.74 (q, C(9)); 24.05 (q, C(10)); 27.65*** (t, C(5)); 30.31*** (t, C(4)); 53.65 (d, C(6)); 113.41 (t, C(8)); 126.94 (d, C(2)); 143.07 (s, C(7)); 160.41 (s, C(3)); 198.35 (s, C(1)).

(±)-2,6,6-Trimethylbicyclo[3.1.1]hept-2-en-4-one (25) (verbenone). The reaction of oxime **22** (150 mg, 0.90 mmol) with $NaNO_2$ (235 mg, 3.60 mmol) and AcOH (0.5 mL) in MeOH (5 mL) was carried out according to procedure *A* for 4 h. Chromatography afforded ketone **25** as a pale-yellow oil (72 mg, 0.48 mmol, 53%).

The reaction of oxime **22** (150 mg, 0.90 mmol) with $NaNO_2$ (130 mg, 1.99 mmol) in AcOH (3 mL) was carried out according to procedure *B* for 1 h. Chromatography afforded ketone **25** as a pale-yellow oil (64 mg, 0.43 mmol, 47%). ^{1}H NMR ($CDCl_3$), δ: 0.90 (s, 3 H, $H_3C(8)$); 1.39 (s, 3 H, $H_3C(9)$); 1.91 (d, 3 H, C(2)Me, $J = 1.8$ Hz); 1.96 (d, 1 H,

H(7α), J = 9.2 Hz); 2.35 (ddd, 1 H, H(1), $J_1 = J_2$ = 5.5 Hz, J_3 = 1.8 Hz); 2.55 (ddd, 1 H, H(5), $J_1 = J_2$ = 5.5 Hz, J_3 = 1.8 Hz); 2.70 (ddd, 1 H, H(7β), J_1 = 9.2 Hz, $J_2 = J_3$ = 5.5 Hz); 5.61 (ddq, 1 H, H(3), $J_1 = J_2 = J_3$ = 1.8 Hz). ^{13}C NMR ($CDCl_3$), δ: 21.73 (q, C(8)); 23.21 (q, C(10)); 26.28 (q, C(9)); 40.51 (t, C(7)); 49.46 (d, C(1)); 53.68 (s, C(6)); 57.32 (d, C(5)); 120.86 (d, C(3)); 169.86 (s, C(2)); 203.58 (s, C(4)).

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