Selective Oxyfunctionalization of Ketones Using 1-Oxopiperidinium Salt

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4-Methoxy-2,2,6,6-tetramethyl-1-oxopiperidinium chloride, made from the corresponding 1-piperidinyloxyl radical and chlorine gas, was used as an oxyfunctionalizing reagent for a number of enolizable ketones. Regioselective α- or γ-oxygenated carbonyl compounds were obtained smoothly at ambient temperature in moderate to good yields. Oxyfunctionalization of (+)-carvone and (−)-carvone proceeded stereoselectively, and provided *cis*-product (5*R*, 6*S*)- and (5*S*, 6*R*)-2-cyclohexen-1-ones, respectively. Interestingly, unsymmetrical ketones afforded isomeric α- and α'-oxygenated ketones, while allyl ketones gave the regiospecific γ-oxygenated products with the migration of the double bond in the allylic group.

1-Oxopiperidinium salts are finding increasing applications in organic chemistry, where they function as mild and selective oxidants for oxidizing the alcohols to their corresponding aldehydes or ketones,[1] and diols to their corresponding lactones.[2] Golubev et al.[3] firstly reported the reaction of 2,2,6,6-tetramethyl-1-oxopiperidinium chloride with a few simple ketones in acetonitrile to produce α-dicarbonyl compounds in reasonable yields; in the case of acetone, the α-oxygenated product has been isolated and characterized. Years later, Hunter et al.[4] studied 1-oxopiperidinium salt as an oxidizing agent and reacted cholestan-3-one with two molar amounts of the salt and a catalytic amount of *p*-toluenesulfonic acid to give cholestan-2,3-dione. Recently, Torii et al.[5] developed a new oxidizing system composed of $RuCl_2(PPh_3)_3$ as a catalyst, molecular oxygen, and 4-benzoyloxy-2,2,6,6-tetramethyl-1-piperidinyloxyl radical for one-pot conversion of aliphatic alcohols to the corresponding α-oxygenated aldehydes. We recently reported that 4-methoxyl-2,2,6,6-tetramethyl-1-oxopiperidinium chloride, derived from corresponding 1-piperidinyloxyl radical by one-electron reaction with chlorine gas, provided an effective methodology for conversion of a range of monoketones bearing an α-methylene group into their corresponding 1,2-diketones.[6] The pathway by which these transformations occur involved attack of the enol at the $\overset{+}{\rangle}\!\!N{=}O$ bond of 1-oxopiperidinium salt that led to the formation of α-oxygenated ketones, then followed by thermal elimination of piperidine conjugative acid in the presence of an equivalent molar amount of *p*-TsOH. The discovery of chemoselective oxyfunctionalization reaction of carbonyl compounds with 1-oxopiperidinium salt in the preliminary studies[3—6] as well as the potential importance of the oxygen functionality ketones for the synthesis of dicabonyl compounds or α-hydroxy ketones have prompted us to further investigate the scope of the title transformation.

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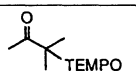
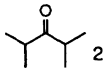
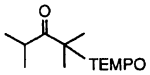
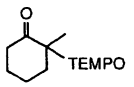
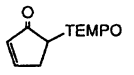
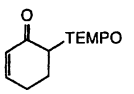
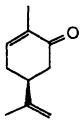
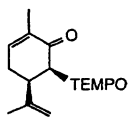
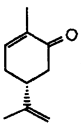
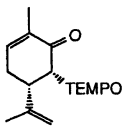
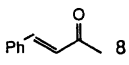
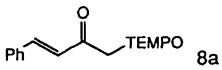
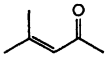
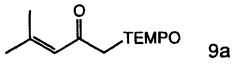
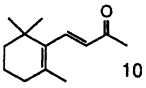
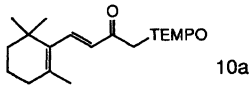
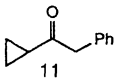
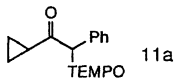
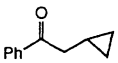
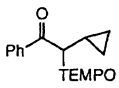
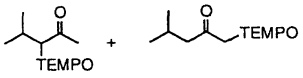
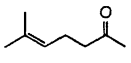
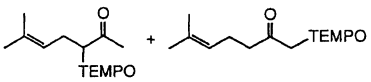
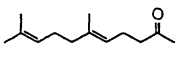
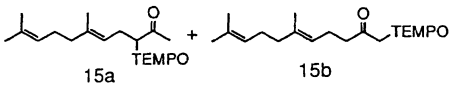
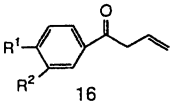
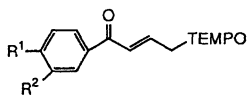
Results and Discussion

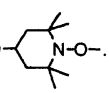
A mixture of 1-oxopiperidinium salt and ketone was stirred in anhydrous acetonitrile under argon atmosphere. With this simple procedure, the various types of oxyfunctionalized ketones were furnished in moderate to good yields. The scope of the reaction is shown in Table 1. The present method is applicable to a variety of ketones bearing olefinic, alkyl, phenyl, or cyclopropyl groups.

Owing to the hydroscopicity of the 1-oxopiperidinium chloride, anhydrous solvent was used in our reaction system. Double bonds adjacent to the carbonyl group seemed not to interfere with the reaction, although there were some problems with α,β-unsaturated cyclic ketones (**4**, **5**, **6**, and **7**) which gave only moderate yields. The reactions of α,β-unsaturated cyclic ketones underwent the oxyfunctionalization rather slowly and suffered from both the electron-deficient double bond and limited structure flexibility. Efforts to increase the yields of α,β-unsaturated cyclic ketones by prolonging the reaction time and raising the temperature were futile. Addition of *p*-TsOH to these reactions somewhat accelerated these transformations, but without changing the yields. It is interesting to note that kinetically controlled stereospecific oxyfunctionalizations were achieved with both **6** and **7**. The structures of product **6a** and **7a** were established on basis of ^{1}H NMR. In case of **6a**, the small coupling constant $J_{H(5)H(6)} = 2.5$ Hz of the ring proton at C-6 indicates that it is an axial-equatorial coupling and that the piperidinyloxy group (TEMPO) is axial orientated. Similarly, in the case of **7a**, the axial C-6 piperidinyloxy group configuration was assigned from the vacinal coupling pattern of the equatorial proton attached to C-6 at $\delta = 4.14$ (d, $J = 2.8$ Hz).

A series of unsymmetrical ketones were involved to gain

Table 1. Reaction of 4-Methoxy-2,2,6,6-tetramethyl-1-oxopiperidinium Chloride with Ketones

Ketone	Reaction time (h)	Oxyfunctionalized product[a)]	Yield%[b,c)]
 1	18	 1a	78
 2	12	 2a	86
 3	71	 3a	72
 4	72	 4a	45
 5	72	 5a	36
 6	72	 6a	32
 7	72	 7a	30
 8	12	 8a	71
 9	24	 9a	82
 10	24	 10a	42
 11	12	 11a	92
 12	18	 12a	89
 13	18	 13a 13b	72 (3.6:1)
 14	18	 14a 14b	82 (13.2:1)
 15	24	 15a 15b	53 (3.2:1)
 16			
a: R^1=H R^2=H	54	17a	76
b: R^1=Cl R^2=H	48	17b	72
c: R^1=Br R^2=H	48	17c	62
d: R^1=Me R^2=H	48	17d	86
e: R^1=MeO R^2=H	48	17e	78
f: R^1=MeO R^2=MeO	48	17f	65

a) TEMPO:  b) Yield of isolated product by flash column chromatography. c) Figure in parentheses refer to the ratios of isomers (determined by ^{1}H NMR).

better understanding of the regioselectivity toward the oxyfunctionalization process. Interestingly, ketones **1**, **3**, and **11** afforded only the regiospecific isomers **1a**, **3a**, and **11a** respectively. Cyclopropyl moiety of both **11** and **12** was tolerated under these conditions. The effect of phenyl group on the oxyfunctionalization of benzyl cyclopropyl ketone (**11**) was significant. The nearly quantitative yield of **11** can be ascribed to the conjugation stabilization of the phenyl group with a double bond in its enol form. For ketones (**13**, **14**, and **15**) having both methyl and methylene group at the α- and α'-position, oxyfunctionalization at the methylene site was favored. The two-site regioisomers could not be separated by column chromatography ratios of the regioisomers were determined by ^{1}H NMR. The observed regioselectivity can be explained by the predominance of the hyperconjugative effect over the steric effect in the enolization process. Golubev et al.[7] proposed this mechanism for the oxyfunctionalization (Scheme 1).

The enol form of the ketone reacted with the 1-oxopiperidinium to give the α-oxygenated carbonyl compounds which underwent one sort of ene reaction. We examined the oxyfunctionalization reaction of 2-adamantanone, which contains an α-C–H group at the bridge-head position that cannot enolize we found that it did not react with the 1-oxopiperidinium salt.

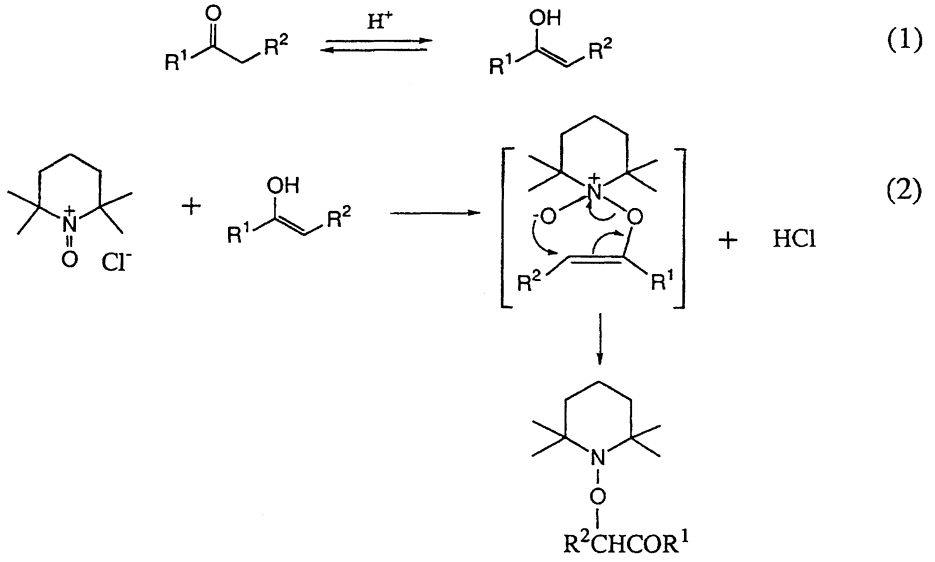
Under identical experimental conditions, the reactions of allyl ketones **16a—f** with 1-oxopiperidinium salt furnished the γ-oxyfunctionalized products **17a—f** together with a small amount of 4-methoxy-2,2,6,6-tetramethyl-1-piperidinyloxyl radical. With these results in hand, the enol form in Eq. 1 (Scheme 1) becomes widely acceptable. However, the absence of α-position oxygenated products during the rearrangement of allyl ketones **16a—f** clearly demonstrates that the five-membered intermediate in Eq. 2 is questionable. It is well-known that 1-oxopiperidinium salt can undergo initially one-electron oxidation with versatile substrates such as phenothiazine,[8] phenol,[9] benzyl ether,[10] bilirubin,[11] tetrathiafulvalene,[12] and papaverine.[13] Enol radical cation can be generated by the oxidizing enol using tris(4-bromophenyl)ammonium hexachloroantimonate.[14] These facts suggest that the rearrangement reaction occurs in a different way. The strong preference for γ-C oxygenation rather than α-C oxygenation may account for the radical cation-mediated reaction (Scheme 2).

Although we did not specifically probe the mechanism, it is likely that 1-oxopiperidinium salt could undergo initially one-electron oxidation with enol. The enol radical cation **16a**$^{+\bullet}$ (Scheme 2), which was formed in the one-electron oxidation step, was expected to deprotonate rapidly subsequently the double bond rearrangement would thus provide a γ-carbonyl free radical. The carbon-centered radical was trapped by the 4-methoxy-2,2,6,6-tetramethyl-1-piperdinyloxy radical to afford the γ-oxygenated product **17a**.

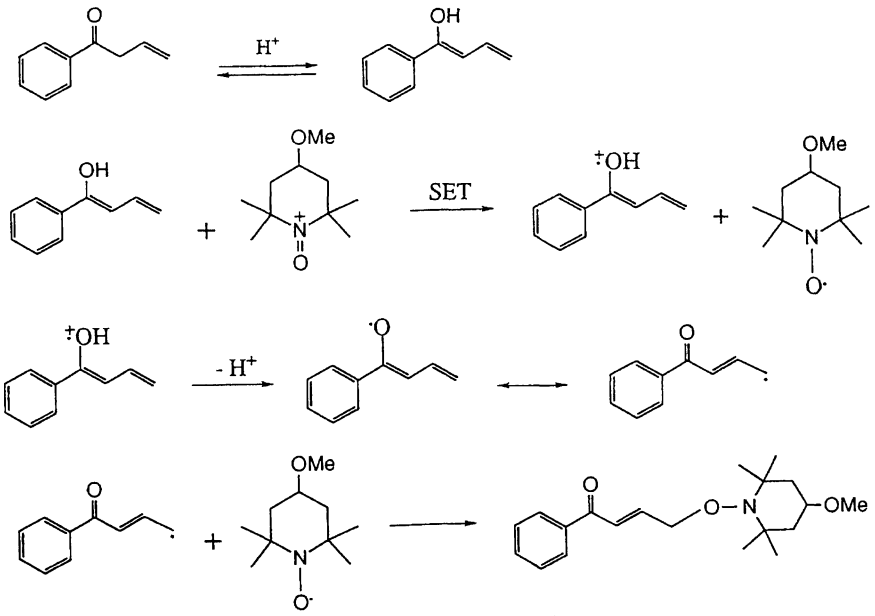
In summary, 4-methoxy-2,2,6,6-tetramethyl-1-piperidinium chloride is an easily prepared oxidizing reagent that reacts with a variety of enolizable ketones to form α- or γ-oxyfunctionalized carbonyl compounds in moderate to good yields. The present approach is especially useful for selective introduction of an oxygen functionality toward unsymmetrical ketones. The regiospecific behavior of γ-oxygenated products **17a—f** derived from allyl ketones **16a—f** should be of interest in both physical organic and synthetic chemistry. Further work concerning synthetic application of the products is underway.

Experimental

Instrumentation. ^{1}H NMR and ^{13}C NMR spectra were taken on a Bruker AM400 NMR spectrometer using $CDCl_3$ as solvent and TMS as reference. DEPT 135 and DEPT 90 pulse sequences were used to aid spectral interpretation. Mass spectra were determined using a VG analytical ZAB-HS mass spectrometer with an ionization potential of 70 eV. Fast atom bombardment (FAB) samples were prepared using 3-nitrobenzyl alcohol as matrix. Infrared spectra were recorded with a Nicolet FT-170SX spectrometer. Melting points were uncorrected. Elemental analyses were carried out with



Scheme 1.



Scheme 2.

an Italian 1106 analyzer.

Materials. 4-Methoxy-2,2,6,6-tetramethyl-1-oxopiperidinium chloride was prepared according to the literature.[15] Most of the starting ketones **1**—**10**, and **13**—**15** were commercial products (Fluka) that were used without purification. Ketones **11**[16] and **16a**—**f**[17] were prepared as described in the literature. Ketone **12** was synthesized by oxidation of 2-cyclopropyl-1-phenyl-ethanol[18] with 2 molar amounts of pyridinium dichromate[19] in anhydrous dichloromethane. All prepared starting ketones had IR, ^{1}H NMR and mass spectra consistent with the proposed structures. MeCN was dried and distilled from CaH_2 before use.

General Procedure. A mixture of the monoketone (3 mmol) and 4-methoxy-2,2,6,6-tetramethyl-1-oxopiperidinium chloride (3.6 mmol) in dry acetonitrile (20 ml) under positive pressure of argon was stirred at ambient temperature. The color of the reaction mixture changed gradually from deep red to light yellow. The progress of the reaction was monitored by TLC. The reaction mixture was poured into water and neutralized with 5% aqueous $NaHCO_3$, and then extracted with chloroform (2×50 ml). The organic layer was washed with brine, dried, and evaporated. The reaction products were obtained by column chromatography on silica gel 200—300 mesh with EtOAc/petroleum ether (from 5 : 100 to 25 : 100) as eluant. The solid products were crystallized from hexane/chloroform.

3-(4-Methoxy-2,2,6,6-tetramethyl-1-piperidinyloxy)-3-methyl-2-butanone (1a): Mp 62—63 °C. IR 2976, 2939, 1717 (s, C=O), 1467, 1378, 1099 cm^{-1}. ^{1}H NMR δ = 3.36 (tt, J = 11.4, 4.1 Hz, 1H), 3.23 (s, 3H, CH_3O), 2.20 (s, 3H, CH_3), 1.81 (m, 2×H$_e$), 1.27 (m, 2×H$_a$), 1.27 (s, 6H, 2×CH_3), 1.11 (s, 6H, 2×CH_3), 0.94 (s, 6H, 2×CH_3). ^{13}C NMR δ_C = 210.8, 85.7, 71.3, 59.6 (2 carbons), 55.5, 45.1 (2 carbons), 33.5 (2 carbons), 23.0 (2 carbons), 24.3, 21.2 (2 carbons). MS m/z (FAB) 272 (M^+ + 1), 256 ($M^+ - CH_3$), 240 ($M^+ - CH_3O$), 186, 170. Found: C, 66.41; H, 10.82; N, 5.21%. Calcd for $C_{15}H_{29}NO_3$: C, 66.38; H, 10.77; N, 5.16%.

2-(4-Methoxy-2,2,6,6-tetramethyl-1-piperidinyloxy)-2,4-dimethyl-3-pentanone (2a): Colorless oil. IR 2975, 2939, 1713 (s, C=O), 1469, 1378, 1099 cm^{-1}. ^{1}H NMR δ_H = 3.45 (tt, J = 11.4, 4.1 Hz, 1H), 3.41 (q, J = 6.8 Hz, 1H), 3.32 (s, 3H, CH_3O), 1.90 (m, 2×H$_e$), 1.40 (s, 6H, 2×CH_3), 1.40—1.36 (m, 2×H$_a$), 1.20 (s, 6H, 2×CH_3), 1.13 (d, J = 6.8 Hz, 6H, 2×CH_3), 1.05 (s, 6H, 2×CH_3). ^{13}C NMR δ_C = 216.9, 86.0, 71.3, 59.6 (2 carbons), 55.5, 45.1 (2 carbons), 34.0, 33.5 (2 carbons), 23.8 (2 carbons), 21.4 (2 carbons), 20.6, 20.5. MS m/z (FAB) 300 (M^+ + 1), 284 ($M^+ - CH_3$), 268 ($M^+ - CH_3O$), 186. Found: C, 68.22; H, 11.03; N, 4.52%. Calcd for $C_{17}H_{33}NO_3$: C, 68.18; H, 11.11; N, 4.68%.

2-(4-Methoxy-2,2,6,6-tetramethyl-1-piperidinyloxy)-2-methyl-cyclohexanone (3a): Mp 46—48 °C. IR 2975, 2939, 1716 (s, C=O), 1469, 1370, 1176, 1099 cm^{-1}. ^{1}H NMR δ_H = 3.44 (tt, J = 11.4, 4.0 Hz, 1H), 3.31 (s, 3H, CH_3O), 3.10—3.04 (m, 1H), 2.35—2.28 (m, 1H), 2.10—2.00 (m, 2H), 1.94—1.84 (m, 2×H$_e$), 1.65—1.40 (m, 4H), 1.38—1.30 (m, 2×H$_a$), 1.29 (s, 3H, CH_3), 1.24 (s, 3H, CH_3), 1.16 (s, 3H, CH_3), 1.14 (s, 3H, CH_3), 0.84 (s, 3H, CH_3). MS m/z (FAB) 298 (M^+ + 1), 282 ($M^+ - CH_3$), 186. Found: C, 68.58; H, 10.42; N, 4.65%. Calcd for $C_{17}H_{31}NO_3$: C, 68.65; H, 10.50; N, 4.71%.

5-(4-Methoxy-2,2,6,6-tetramethyl-1-piperidinyloxy)-2-cyclopenten-1-one (4a): Mp 98—99 °C. IR 2971, 2935, 1717 (s, C=O), 1584, 1454, 1377, 1173, 1099, 970, 762 cm^{-1}. ^{1}H NMR δ_H = 7.50 (dt, J = 6.3, 2.8 Hz, 1H, CH=C<u>H</u>CH$_2$), 6.14 (dt, J = 6.3, 1.9 Hz, 1H, C<u>H</u>=CHCH$_2$), 4.62 (dd, J = 6.6, 3.5 Hz, 1H), 3.44 (tt, J = 11.4, 4.1 Hz, 1H), 3.32 (s, 3H, CH_3O), 3.05 (dm, J = 18.1 Hz, 1H, C<u>H$_A$H$_B$</u>), 2.77 (dm, J = 18.1 Hz, 1H, CH$_A$<u>H$_B$</u>), 1.88 (m, 2×H$_e$), 1.39 (s, 3H, CH_3), 1.37 (m, 2×H$_a$), 1.30 (s, 3H, CH_3), 1.20 (s, 3H, CH_3), 1.14 (s, 3H, CH_3). ^{13}C NMR δ_C = 205.4, 159.3, 132.3, 85.3, 71.5, 61.3, 59.5, 55.7, 45.3, 45.1, 37.0, 34.4, 32.3, 21.3, 21.2. MS m/z (EI %) 267 (M^+; 8), 252 ($M^+ - CH_3$; 30), 186 (100). Found: C, 67.42; H, 9.34; N, 5.29%. Calcd for $C_{15}H_{25}NO_3$: C, 67.38; H, 9.43; N, 5.24%.

6-(4-Methoxy-2,2,6,6-tetramethyl-1-piperidinyloxy)-2-cyclohexen-1-one (5a): Mp 77—78 °C. IR 2974, 2936, 1690 (s, C=O), 1378, 1096, 980, 758 cm^{-1}. ^{1}H NMR δ_H = 6.89 (dt, J = 10, 4.0 Hz, 1H, CH=C<u>H</u>CH$_2$), 5.98 (dt, J = 10, 2.0 Hz, 1H, C<u>H</u>=CHCH$_2$), 4.28 (dd, J = 8.7, 3.7 Hz, 1H), 3.44 (tt, J = 11.6, 4.2 Hz, 1H), 3.32 (s, 3H, CH_3O), 2.57 (m, 1H), 2.36 (m, 2H), 2.16 (m, 1H), 1.85 (m, 2×H$_e$), 1.41 (dd, J = 12.4, 11.6 Hz, 1H$_a$), 1.38 (dd, J = 12.4, 11.6 Hz, 1H$_a$), 1.23 (s, 6H, 2×CH_3), 1.19 (s, 3H, CH_3), 1.08 (s, 3H, CH_3). ^{13}C NMR δ_C = 197.8, 149.0, 128.9, 84.2, 71.6, 60.7, 60.2, 55.7, 45.0 (2 carbons), 34.4, 33.8, 29.7, 24.4, 21.3 (2 carbons). MS m/z (FAB) 282 (M^+ + 1), 266 ($M^+ - CH_3$), 186. Found: C, 68.35;

H, 9.56; N, 4.83%. Calcd for $C_{16}H_{27}NO_3$: C, 68.29; H, 9.67; N, 4.98%.

(5*R*,6*S*)-5-Isopropenyl-6-(4-methoxy-2,2,6,6-tetramethyl-1-piperidinyloxy)-2-methyl-2-cyclohexen-1-one (6a): Mp 66—68 °C. IR 2975, 2937, 1628 (s, C=O), 1453, 1376, 1169, 1096, 896, 743 cm^{-1}. ^1H NMR δ_H = 6.61 (dd, J = 3.6, 1.6 Hz, 1H, $CH_2C\underline{H}$=), 4.85 (s, 1H), 4.67 (s, 1H), 4.17 (d, J = 2.5 Hz, 1H), 3.44 (tt, J = 11.2, 4.0 Hz, 1H), 3.32 (s, 3H, CH_3O), 3.11 (m, 1H), 2.88 (dm, J = 19 Hz, 1H), 2.34 (dm, J = 19 Hz, 1H), 1.83 (m, 2×H_e), 1.77 (s, 3H, CH_3), 1.75 (s, 3H, CH_3), 1.41 (dd, J = 12.4, 11.2 Hz, 1H_a), 1.39 (dd, J = 12.4, 11.2 Hz, 1H_a), 1.32 (s, 3H, CH_3), 1.22 (s, 3H, CH_3), 1.09 (s, 3H, CH_3), 0.93 (s, 3H, CH_3). ^{13}C NMR δ_C = 197.6, 141.8, 141.5, 133.6, 112.4, 85.3, 71.3, 60.6, 59.3, 55.4, 46.2, 44.3 (2 carbons), 33.7, 33.4, 26.3, 22.3, 21.1, 20.8, 15.6. MS m/z (FAB) 336 (M^+ + 1), 320 ($M^+ - CH_3$), 186. Found: C, 71.54; H, 9.81; N, 4.23%. Calcd for $C_{20}H_{33}NO_3$: C, 71.60; H, 9.91; N, 4.18%.

(5*S*,6*R*)-5-Isopropenyl-6-(4-methoxy-2,2,6,6-tetramethyl-1-piperidinyloxy)-2-methyl-2-cyclohexen-1-one (7a): Mp 66—68 °C. IR 2975, 2938, 1683 (s, C=O), 1453, 1376, 1169, 1098, 895 cm^{-1}. ^1H NMR δ_H 6.59 (dd, J = 3.6, 1.5 Hz, 1H, $CH_2C\underline{H}$=), 4.82 (s, 1H), 4.64 (s, 1H), 4.14 (d, J = 2.8 Hz, 1H), 3.40 (tt, J = 11.3, 4.1 Hz, 1H), 3.29 (s, 3H, CH_3O), 3.08 (m, 1H), 2.85 (dm, J = 19.1 Hz, 1H), 2.31 (dm, J = 19.1 Hz, 1H), 1.81 (m, 2×H_e), 1.74 (s, 3H, CH_3), 1.72 (s, 3H, CH_3), 1.46 (dd, J = 12.4, 11.3 Hz, 1H_a), 1.36 (dd, J = 12.4, 11.3 Hz, 1H_a), 1.29 (s, 3H, CH_3), 1.19 (s, 3H, CH_3), 1.12 (s, 3H, CH_3), 0.90 (s, 3H, CH_3). ^{13}C NMR δ_C = 197.6, 141.9, 141.6, 133.8, 112.6, 85.5, 71.5, 60.8, 59.5, 55.5, 46.4, 44.5 (2 carbons), 33.9, 33.5, 26.4, 22.0, 21.2, 20.9, 15.7. MS m/z (FAB) 336 (M^+ + 1), 320 ($M^+ - CH_3$), 186. Found: C, 71.45; H, 9.88; N, 4.13%. Calcd for $C_{20}H_{33}NO_3$: C, 71.60; H, 9.91; N, 4.18%.

(*E*)-1-(4-Methoxy-2,2,6,6-tetramethyl-1-piperidinyloxy)-4-phenyl-3-buten-2-one (8a): Mp 78—79 °C. IR 2974, 2939, 1686 (s, C=O), 1608, 1375, 1097, 976, 750 cm^{-1}. ^1H NMR δ_H = 7.68 (d, J = 16 Hz, 1H), 7.57 (m, 2H, ArH), 7.40 (m, 3H, ArH), 7.03 (d, J = 16 Hz, 1H), 4.64 (s, 2H, CH_2), 3.46 (tt, J = 11.2, 4.1 Hz, 1H), 3.32 (s, 3H, CH_3O), 1.89 (dd, J = 12.5, 4.1 Hz, 2×H_e), 1.39 (dd, J = 12.5, 11.2 Hz, 2×H_a), 1.25 (s, 6H, 2×CH_3), 1.21 (s, 6H, CH_3). ^{13}C NMR δ_C = 196.6, 143.3, 134.5, 130.6, 128.9 (2 carbons), 128.4 (2 carbons), 122.0, 82.7, 71.5, 60.2 (2 carbons), 55.7, 44.5 (2 carbons), 33.0 (2 carbons), 21.2 (2 carbons). MS m/z (EI %) 331 (M^+; 20), 316 ($M^+ - CH_3$; 83), 186 (100). Found: C, 72.51; H, 8.69; N, 4.32%. Calcd for $C_{20}H_{29}NO_3$: C, 72.47; H, 8.82; N, 4.23%.

1-(4-Methoxy-2,2,6,6-tetramethyl-1-piperidinyloxy)-4-methyl-3-penten-2-one (9a): Mp 59—60 °C. IR 2966, 2937, 1698 (s, C=O), 1621, 1377, 1099, 765 cm^{-1}. ^1H NMR δ_H = 6.26 (s, 1H, CH=), 4.42 (s, 2H, CH_2), 3.45 (tt, J = 11.3, 4.1 Hz, 1H), 3.33 (s, 3H, CH_3O), 2.39 (s, 3H, CH_3), 1.94 (s, 3H, CH_3), 1.87 (dd, J = 12.4, 4.1 Hz, 2×H_e), 1.37 (dd, J = 12.4, 11.3 Hz, 2×H_a), 1.22 (s, 6H, 2×CH_3), 1.18 (s, 6H, 2×CH_3) ^{13}C NMR δ_C = 197.1, 157.5, 120.1, 83.6, 71.6, 60.2 (2 carbons), 55.8, 44.5 (2 carbons), 33.0 (2 carbons), 28.1, 21.2 (3 carbons). MS m/z (FAB) 284 (M^+ + 1), 268 ($M^+ - CH_3$), 252 ($M^+ - CH_3O$), 186, 170. Found: C, 68.02; H, 10.45; N, 4.82%. Calcd for $C_{16}H_{29}NO_3$: C, 67.81; H, 10.31; N, 4.94%.

(*E*)-1-(4-Methoxy-2,2,6,6-tetramethyl-1-piperidinyloxy)-4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-buten-2-one (10a): Mp 62—64 °C. IR 2971, 2934, 1686 (s, C=O), 1582, 1459, 1360, 1099, 977 cm^{-1}. ^1H NMR δ_H = 7.48 (d, J = 16.4 Hz, 1H), 6.49 (d, J = 16.4 Hz, 1H), 4.52 (s, 2H, CH_2), 3.43 (tt, J = 11.4, 4.2 Hz, 1H), 3.30 (s, 3H, CH_3O), 2.07 (t, J = 6.0 Hz, 2H), 1.86 (dd, J = 12.3, 4.2 Hz, 2×H_e), 1.80 (s, 3H, CH_3), 1.60 (m, 2H), 1.46 (m, 2H), 1.39 (dd, J = 12.3, 11.4 Hz, 2×H_a), 1.19 (s, 6H, 2×CH_3), 1.18 (s, 6H, 2×CH_3), 1.08 (s, 6H, 2×CH_3). ^{13}C NMR δ_C = 197.0, 142.8, 138.2, 136.4, 125.7, 82.8, 71.6, 60.3 (2 carbons), 55.8, 44.5 (2 carbons), 40.2, 34.1, 33.9, 33.0 (2 carbons), 28.8 (2 carbons), 21.8, 21.2 (2 carbons), 18.8. MS m/z (FAB) 378 (M^+ + 1), 362 ($M^+ - CH_3$), 346 ($M^+ - CH_3O$), 186. Found: C, 73.21; H, 10.33; N, 3.82%. Calcd for $C_{23}H_{39}NO_3$: C, 73.16; H, 10.41; N, 3.71%.

1-Cyclopropyl-2-(4-methoxy-2,2,6,6-tetramethyl-1-piperidinyloxy)-2-phenylethanone (11a): Colorless oil. IR 2972, 1700 (s, C=O), 1415, 1379, 1098, 869 cm^{-1}. ^1H NMR δ_H = 7.41 (d, J = 7.2 Hz, 2H, ArH), 7.31—7.24 (m, 3H, ArH), 5.19 (s, 1H), 3.44 (tt, J = 11.4, 4.1 Hz, 1H), 3.29 (s, 3H, CH_3O), 2.34 (m, 1H), 1.99 (dd, J = 12.4, 4.1 Hz, 1H_e), 1.82 (dd, J = 12.4, 4.1 Hz, 1H_e), 1.39 (dd, J = 12.4, 11.4 Hz, 1H_a), 1.31 (s, 3H, CH_3), 1.25 (dd, J = 12.4, 11.4 Hz, 1H_a), 1.19 (s, 3H, CH_3), 1.18 (s, 3H, CH_3), 0.86 (m, 2H), 0.81 (m, 2H), 0.74 (s, 3H, CH_3). ^{13}C NMR δ_C = 208.7, 137.9, 128.1 (2 carbons), 127.5, 126.5 (2 carbons), 95.6, 71.2, 59.9, 59.6, 55.4, 44.6 (2 carbons), 33.4, 33.0, 21.1, 20.9, 16.7, 12.5, 10.7. MS m/z (FAB) 346 (M^+ + 1), 186. Found: C, 73.04; H, 8.99; N, 4.10%. Calcd for $C_{21}H_{31}NO_3$: C, 73.01; H, 9.05; N, 4.05%.

2-Cyclopropyl-2-(4-methoxy-2,2,6,6-tetramethyl-1-piperidinyloxy)-1-phenylethanone (12a): Colorless oil. IR 2973, 1679 (s, C=O), 1449, 1379, 1271, 1098, 761 cm^{-1}. ^1H NMR δ_H = 8.15 (d, J = 7.7 Hz, 2H, ArH), 7.57 (t, J = 7.4 Hz, 1H, ArH), 7.47 (dd, J = 7.7, 7.4 Hz, 2H, ArH), 4.22 (d, J = 8.7 Hz, 1H), 3.43 (tt, J = 11.4, 4.0 Hz, 1H), 3.30 (s, 3H, CH_3O), 1.92 (dd, J = 12.5, 4.0 Hz, 1H_e), 1.79 (dd, J = 12.5, 4.0 Hz, 1H_e), 1.47 (s, 3H, CH_3), 1.41 (dd, J = 12.5, 11.4 Hz, 1H_a), 1.33 (dd, J = 12.5, 11.4 Hz, 1H_a), 1.28 (s, 3H, CH_3), 1.23 (m, 1H), 1.02 (s, 3H, CH_3), 0.93 (s, 3H, CH_3), 0.77 (m, 1H), 0.58 (m, 1H), 0.45 (m, 1H), 0.27 (m, 1H). ^{13}C NMR δ_C = 198.6, 135.4, 132.8, 129.6 (2 carbons), 128.4 (2 carbons), 95.2, 71.6, 60.3, 60.2, 55.7, 49.2 (2 carbons), 34.4, 33.9, 21.5, 21.1, 14.9, 8.6, 2.1. MS m/z (FAB) 346 (M^+ + 1), 186. Found: C, 73.08; H, 8.94; N, 4.11%. Calcd for $C_{21}H_{31}NO_3$: C, 73.01; H, 9.05; N, 4.05%.

3-(4-Methoxy-2,2,6,6-tetramethyl-1-piperidinyloxy)-4-methyl-2-pentanone (13a Major Isomer): IR 2975, 2939, 1713 (s, C=O), 1469, 1378, 1099 cm^{-1}. ^1H NMR δ_H = 4.03 (d, J = 6.0 Hz, 1H), 3.43 (tt, J = 11.3, 4.1 Hz, 1H), 3.28 (s, 3H, CH_3O), 2.19 (s, 3H, CH_3), 1.85 (m, 2×H_e), 1.35 (m, 2×H_a), 1.26 (s, 6H, 2×CH_3), 1.21 (s, 6H, 2×CH_3), 1.01 (m, 1H), 0.91 (d, J = 7.3 Hz, 3H, CH_3), 0.90 (d, J = 7.3 Hz, 3H, CH_3). ^{13}C NMR δ_C = 210.1, 94.4, 71.5, 60.2, 59.9, 55.0, 45.3, 44.9, 34.6, 33.9, 30.3, 29.6, 21.4, 21.1, 18.9, 16.7. MS m/z (FAB) 286 (M^+ + 1), 270 ($M^+ - CH_3$), 186.

3-(4-Methoxy-2,2,6,6-tetramethyl-1-piperidinyloxy)-6-methyl-5-hepten-2-one (14a Major Isomer): IR 2974, 2935, 1717 (s, C=O), 1377, 1173, 1099, 973, 762 cm^{-1}. ^1H NMR δ_H = 4.98 (t, J = 7.4 Hz, 1H), 4.06 (dd, J = 9.3, 4.3 Hz, 1H), 3.44 (tt, J = 11.4, 4.2 Hz, 1H), 3.29 (s, 3H, CH_3O), 2.58 (m, 1H), 2.41 (m, 1H), 2.12 (s, 3H, CH_3), 1.82 (m, 2×H_e), 1.65 (s, 3H, CH_3), 1.55 (s, 3H, CH_3), 1.35 (m, 2×H_a), 1.25 (s, 3H, CH_3), 1.17 (s, 6H, 2×CH_3), 1.01 (s, 3H, CH_3). ^{13}C NMR δ_C = 210.2, 134.9, 117.6, 90.9, 71.5, 60.2 (2 carbons), 55.7, 45.0 (2 carbons), 34.2, 33.9, 30.6, 27.2, 25.7, 21.2 (2 carbons), 17.9. MS m/z (FAB) 312 (M^+ + 1), 296 ($M^+ - CH_3$), 186.

(*E*)-3-(4-Methoxy-2,2,6,6-tetramethyl-1-piperidinyloxy)-6,10-dimethyl-5,9-undecadien-2-one (15a Major Isomer): IR 2974, 2935, 1717 (s, C=O), 1377, 1137, 1099, 973, 762 cm^{-1}. ^1H NMR δ_H = 6.05—4.95 (m, 2H, 2×CH=), 4.13 (dd, J = 10.2, 4.2 Hz, 1H), 3.40 (tt, J = 11.3, 4.3 Hz, 1H), 3.30 (s, 3H, CH_3O), 2.56—2.55 (m, 1H), 2.50—2.40 (m, 1H), 2.18 (s, 3H, CH_3), 2.05—1.95 (m, 4H), 1.90—1.80 (m, 2×H_e), 1.61 (s, 3H, CH_3), 1.53 (s, 6H, 2×CH_3), 1.40—1.30 (m, 2×H_a), 1.22 (s, 3H, CH_3), 1.18 (s, 3H, CH_3), 1.13

(s, 6H, 2×CH_3). ^{13}C NMR δ_C = 209.9, 138.3, 131.3, 123.9, 117.5, 90.7, 71.4, 60.1, 59.9, 55.6, 44.9, 44.4, 39.5, 34.1, 33.8, 32.9, 30.4, 26.5, 26.4, 21.1, 21.0, 17.5, 16.0. MS *m/z* (FAB) 380 (M^+ + 1), 348 ($M^+ - CH_3O$), 186.

(*E*)-4-(4-Methoxy-2,2,6,6-tetramethyl-1-piperidinyloxy)-1-phenyl-2-buten-1-one (17a): Colorless oil. IR 2976, 2935, 1674 (s, C=O), 1626, 1366, 1286, 1176, 1096, 960, 760 cm^{-1}. ^{1}H NMR δ_H = 7.96 (d, *J* = 7.8 Hz, 2H, ArH), 7.58 (t, *J* = 7.4 Hz, 1H, ArH), 7.48 (dd, *J* = 7.8, 7.4 Hz, 2H, ArH), 7.18 (dt, *J* = 15.7, 1.8 Hz, 1H, C<u>H</u>=CHCH$_2$), 7.02 (dt, *J* = 15.7, 4.0 Hz, 1H, CH=C<u>H</u>CH$_2$), 4.60 (dd, *J* = 4.0, 1.8 Hz, 2H, CH=CHC<u>H$_2$</u>), 3.47 (tt, *J* = 11.4, 4.1 Hz, 1H), 3.34 (s, 3H, CH_3O), 1.89 (dd, *J* = 12.5, 4.1 Hz, 2×H_e), 1.40 (dd, *J* = 12.5, 11.4 Hz, 2×H_a), 1.22 (s, 12H, 4×CH_3). ^{13}C NMR δ_C = 190.5, 144.0, 137.8, 132.7, 128.5 (2 carbons), 128.3 (2 carbons), 124.2, 76.3, 71.6, 60.1 (2 carbons), 55.7, 44.5 (2 carbons), 33.0 (2 carbons), 21.1 (2 carbons). MS *m/z* (FAB) 332 (M^+ + 1), 316 ($M^+ - CH_3$), 186, 170, 145. Found: C, 72.51; H, 8.77; N, 4.13%. Calcd for $C_{20}H_{29}NO_3$: C, 72.47; H, 8.82; N, 4.23%.

(*E*)-1-(4-Chlorophenyl)-4-(4-methoxy-2,2,6,6-tetramethyl-1-piperidinyloxy)-2-buten-1-one (17b): Mp 69—70 °C. IR 2976, 2933, 1674 (s, C=O), 1590, 1376, 1175, 1094, 962 cm^{-1}. ^{1}H NMR δ_H = 7.89 (d, *J* = 8.2 Hz, 2H, ArH), 7.46 (d, *J* = 8.3 Hz, 2H, ArH), 7.13 (dt, *J* = 15.6, 1.6 Hz, 1H, C<u>H</u>=CHCH$_2$), 7.02 (dt, *J* = 15.6, 3.6 Hz, 1H, CH=C<u>H</u>CH$_2$), 4.60 (dd, *J* = 3.6, 1.6 Hz, 2H, CH=CHC<u>H$_2$</u>), 3.46 (tt, *J* = 11.4, 4.1 Hz, 1H), 3.30 (s, 3H, CH_3O), 1.89 (dd, *J* = 12.5, 4.1 Hz, 2×H_e), 1.40 (dd, *J* = 12.5, 11.4 Hz, 2×H_a), 1.22 (s, 6H, 2×CH_3), 1.21 (s, 6H, 2×CH_3). ^{13}C NMR δ_C = 189.0, 144.6, 139.1, 136.0, 129.9 (2 carbons), 128.8 (2 carbons), 123.6, 76.2, 71.6, 60.1 (2 carbons), 55.7, 44.4 (2 carbons), 32.9 (2 carbons), 21.1 (2 carbons). MS *m/z* (FAB) 368 (M^+ + 2 + H), 366 (M^+ + H), 350 ($M^+ - CH_3$), 186, 170. Found: C, 65.67; H, 7.74; N, 3.76%. Calcd for $C_{20}H_{28}ClNO_3$: C, 65.65; H, 7.71; N, 3.83%.

(*E*)-1-(4-Bromophenyl)-4-(4-methoxy-2,2,6,6-tetramethyl-1-piperidinyloxy)-2-buten-1-one (17c): Mp 76—77 °C. IR 2973, 2925, 1668 (s, C=O), 1583, 1368, 1171, 1097, 981 cm^{-1}. ^{1}H NMR δ_H = 7.86 (d, *J* = 8.5 Hz, 2H, ArH), 7.63 (d, *J* = 8.5 Hz, 2H, ArH), 7.12 (d, *J* = 15.6 Hz, 1H, C<u>H</u>=CHCH$_2$), 7.02 (dt, *J* = 15.6, 3.8 Hz, 1H, CH=C<u>H</u>CH$_2$), 4.60 (d, *J* = 3.8 Hz, 2H, CH=CHC<u>H$_2$</u>), 3.45 (tt, *J* = 11.5, 4.0 Hz, 1H), 3.34 (s, 3H, CH_3O), 1.89 (dd, *J* = 12.2, 4.0 Hz, 2×H_e), 1.37 (dd, *J* = 12.2, 11.5 Hz, 2×H_a), 1.22 (s, 12H, 4×CH_3). MS *m/z* (FAB) 412 (M^+ + 2 + H), 410 (M^+ + H), 394 ($M^+ - CH_3$), 378 ($M^+ - CH_3O$), 186. Found: C, 58.41; H, 6.93; N, 3.42%. Calcd for $C_{20}H_{28}BrNO_3$: C, 58.54; H, 6.88; N, 3.41%.

(*E*)-4-(4-Methoxy-2,2,6,6-tetramethyl-1-piperidinyloxy)-1-(4-methylphenyl)-2-buten-1-one (17d): Mp 70—71 °C. IR 2976, 2930, 1669 (s, C=O), 1606, 1361, 1176, 1095, 965, 808 cm^{-1}. ^{1}H NMR δ_H = 7.88 (d, *J* = 8.2 Hz, 2H, ArH), 7.29 (d, *J* = 8.2 Hz, 2H, ArH), 7.16 (dt, *J* = 15.5, 2.0 Hz, 1H, C<u>H</u>=CHCH$_2$), 7.00 (dt, *J* = 15.5 4.0 Hz, 1H, CH=C<u>H</u>CH$_2$), 4.59 (dd, *J* = 4.0, 2.0 Hz, 2H, CH=CHC<u>H$_2$</u>), 3.47 (tt, *J* = 11.6, 4.2 Hz, 1H), 3.38 (s, 3H, CH_3O), 2.45 (s, 3H, CH_3Ar), 1.89 (dd, *J* = 12.4, 4.2 Hz, 2×H_e), 1.40 (dd, *J* = 12.4, 11.6 Hz, 2×H_a), 1.23 (s, 12H, 4×CH_3). ^{13}C NMR δ_C = 190.0, 143.6, 143.5, 132.2, 129.3 (2 carbons), 128.7 (2 carbons), 124.3, 76.5, 71.7, 60.2 (2 carbons), 55.8, 44.5 (2 carbons), 33.0 (2 carbons), 21.6, 21.2 (2 carbons). MS *m/z* (FAB) 346 (M^+ + 1), 330 ($M^+ - CH_3$), 186. Found: C, 72.98; H, 8.94; N, 3.97%. Calcd for $C_{21}H_{31}NO_3$: C, 73.01; H, 9.05; N, 4.05%.

(*E*)-1-(4-Methoxyphenyl)-4-(4-methoxy-2,2,6,6-tetramethyl-1-piperidinyloxy)-2-buten-1-one (17e): Mp 80—82 °C. IR 2975, 2936, 1668 (s, C=O), 1597, 1290, 1172, 1094, 961, 810 cm^{-1}. ^{1}H NMR δ_H = 7.96 (d, *J* = 8.8 Hz, 2H, ArH), 7.16 (dt, *J* = 16.4, 2.0 Hz, 1H, C<u>H</u>=CHCH$_2$), 6.97 (dt, *J* = 16.4, 4.0 Hz, 1H, CH=C<u>H</u>CH$_2$), 6.94 (d, *J* = 8.8 Hz, 2H, ArH), 4.57 (dd, *J* = 4.0, 2.0 Hz, 2H, CH=CHC<u>H$_2$</u>), 3.85 (s, 3H, CH_3OAr), 3.44 (tt, *J* = 11.4, 4.1 Hz, 1H), 3.31 (s, 3H, CH_3O), 1.87 (dd, *J* = 12.6, 4.1 Hz, 2×H_e), 1.38 (dd, *J* = 12.6, 11.4 Hz, 2×H_a), 1.20 (s, 12H, 4×CH_3). ^{13}C NMR δ_C = 188.5, 163.3, 142.8, 130.7 (2 carbons), 130.5, 123.6, 113.7 (2 carbons), 76.3, 71.5, 60.0 (2 carbons), 55.6, 55.3, 44.4 (2 carbons), 33.1, 32.9, 21.0, 20.7. MS *m/z* (FAB) 362 (M^+ + 1), 346 ($M^+ - CH_3$), 186. Found: C, 69.84; H, 8.67; N, 3.94%. Calcd for $C_{21}H_{31}NO_4$: C, 69.77; H, 8.65; N, 3.88%.

(*E*)-1-(3,4-Dimethoxyphenyl)-4-(4-methoxy-2,2,6,6-tetramethyl-1-piperidinyloxy)-2-buten-1-one (17f): Mp 133—135 °C. IR 2973, 2937, 1668 (s, C=O), 1593, 1271, 1166, 1097, 961, 766 cm^{-1}. ^{1}H NMR δ_H = 7.59 (d, *J* = 8.4 Hz, 1H, ArH), 7.55 (s, 1H, ArH), 7.17 (d, *J* = 15.5 Hz, 1H, C<u>H</u>=CHCH$_2$), 6.97 (dt, *J* = 15.5, 4.0 Hz, 1H, CH=C<u>H</u>CH$_2$), 6.90 (d, *J* = 8.4 Hz, 1H, ArH), 4.57 (d, *J* = 4.0 Hz, 2H, CH=CHC<u>H$_2$</u>), 3.94 (s, 3H, CH_3OAr), 3.92 (s, 3H, CH_3OAr), 3.43 (tt, *J* = 11.4, 4.2 Hz, 1H), 3.33 (s, 3H, CH_3O), 1.86 (dd, *J* = 12.1, 4.2 Hz, 2×H_e), 1.35 (dd, *J* = 12.1, 11.4 Hz, 2×H_a), 1.20 (s, 12H, 4×CH_3). MS *m/z* (FAB) 392 (M^+ + 1), 376 ($M^+ - CH_3$), 186. Found: C, 67.52; H, 8.62; N, 3.62%. Calcd for $C_{22}H_{33}NO_5$: C, 67.49; H, 8.50; N, 3.58%.

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