Preparation and Some Reactions of 3-Oxazoline *N*-Oxides

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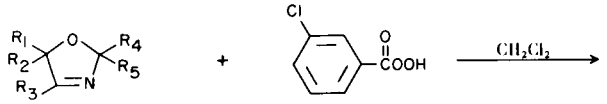
Substituted 3-oxazolines react with *m*-chloroperoxybenzoic acid to give the corresponding 3-oxazoline *N*-oxides. These heterocyclic nitrones underwent molecular rearrangements, but would not react with 1,3-cyclo-addition type reagents.

The synthesis of a wide variety of substituted 3-oxazolines has been accomplished by the reaction of α-hydroxy ketones and aromatic aldehydes with ammonia in yields of 50-95 percent (2,3). No additional work on the chemistry of this new type of heterocycle has been reported. It was found that by treating these 3-oxazolines with *m*-chloroperoxybenzoic acid in methylene chloride, they were converted to the corresponding *N*-oxides in 82-96 percent yields.



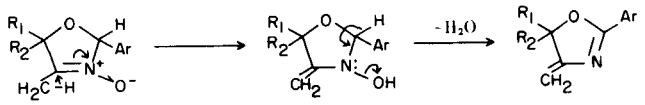
(Table I gives the nitrones thus prepared).

The infrared spectra of these nitrones showed the C=N stretching mode near 1600 cm^{-1}. It was downfield about 30 cm^{-1} from that of the parent 3-oxazoline. The N→O stretching mode was found between 1100 cm^{-1} and 1200 cm^{-1}. Their nmr spectra showed the methyl group at R_3 as a singlet shifted upfield by about 30 cps from that of the corresponding methyl group of the 3-oxazoline. Their mass spectra showed a small p-16 fragment.

Refluxing the nitrones containing 2-aryl substitution in xylene in the presence of magnesium sulfate gave the corresponding 4-methylene-2-oxazolines.

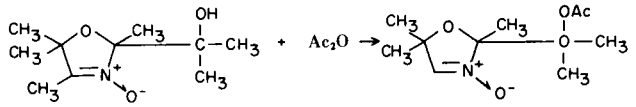
(Table II gives the 2-oxazolines thus prepared).

The infrared spectra of these 2-oxazolines showed the C=N stretching mode at about 1600 cm^{-1} and the C=C stretching mode at about 1550 cm^{-1}. Their nmr spectra showed the methylene protons as two singlets, one at about 5.50 τ and the other at about 5.00 τ. The following mechanism was suggested for the rearrangement of the nitrones to 2-oxazolines.



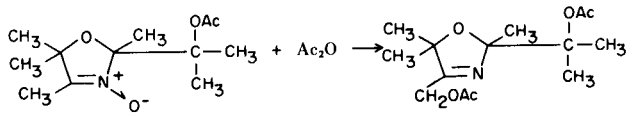
Bromination of 5,5-dimethyl-4-methylene-2-phenyl-2-oxazoline (VIII) gave a solid which analyzed correctly for a dibromo derivative of VIII. Its nmr spectra showed two methylene protons as a singlet at 6.42 τ, which eliminated a ring expansion structure for VIII.

Treatment of 2-(2-hydroxy-2-propyl)-2,4,5,5-tetramethyl-3-oxazoline *N*-oxide (I) with acetic anhydride gave 2-(2-acetoxy-2-propyl)-2,4,5,5-tetramethyl-3-oxazoline *N*-oxide (XI).



I XI

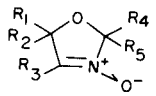
Treatment of XI with a second mole of acetic anhydride gave 2-(2-acetoxy-2-propyl)-4-acetoxymetnyl-2,5,5-trimethyl-3-oxazoline (XII).



XI XII

TABLE I

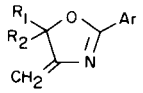
3-Oxazoline *N*-Oxides



Name		Structure	Melting Point	Yield
I.	2-(2-Hydroxy-2-propyl)-2,4,5,5-tetramethyl-3-oxazoline *N*-oxide	$R_1 = R_2 = R_3 = R_4 = CH_3$ $R_5 = C(OH)(CH_3)_2$	77°	96 %
II.	2-Phenyl-4,5,5-trimethyl-3-oxazoline *N*-oxide	$R_1 = R_2 = R_3 = CH_3$ $R_4 = H$, R_5 = phenyl	104°	82 %
III.	2-Furyl-4,5,5-trimethyl-3-oxazoline *N*-oxide	$R_1 = R_2 = R_3 = CH_3$ $R_4 = H$, R_5 = furyl	129°	83 %
IV.	2-(4-Chlorophenyl)-4,5,5-trimethyl-3-oxazoline *N*-oxide	$R_1 = R_2 = R_3 = CH_3$ $R_4 = H$, R_5 = 4-chlorophenyl	264°	92 %
V.	2-(2-Hydroxyphenyl)-4,5,5-trimethyl-3-oxazoline *N*-oxide	$R_1 = R_2 = R_3 = CH_3$ $R_4 = H$, R_5 = 2-hydroxyphenyl	105°	95 %
VI.	4,5-Dimethyl-5-ethyl-2-(4-methoxyphenyl)-3-oxazoline *N*-oxide	$R_1 = R_3 = CH_3$ $R_2 = CH_3CH_2$ $R_4 = H$, R_5 = 4-methoxyphenyl	167°	93 %
VII.	2-(4-Methoxyphenyl)-4,5,5-trimethyl-3-oxazoline *N*-oxide	$R_1 = R_2 = R_3 = CH_3$ $R_4 = H$, R_5 = 4-methoxyphenyl	181°	95 %

TABLE II

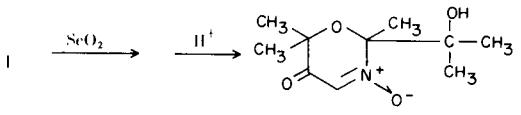
4-Methylene-2-oxazolines



Name		Structure	Boiling Point	Yield
VIII.	5,5-Dimethyl-4-methylene-2-phenyl-2-oxazoline	$R_1 = R_2 = CH_3$ Ar = phenyl	68° (0.05 mm)	96 %
IX.	5,5-Dimethyl-2-(4-methoxyphenyl)-4-methylene-2-oxazoline	$R_1 = R_2 = CH_3$ Ar = 4-methoxyphenyl	81° (0.05 mm)	92 %
X.	5-Ethyl-2-(4-methoxyphenyl)-5-methyl-4-methylene-2-oxazoline	$R_1 = CH_3$ $R_2 = CH_3CH_2$ Ar = 4-methoxyphenyl	78° (0.05 mm)	89 %

The infrared spectrum of XII lacked the N→O stretching mode at 1150 cm^{-1} and contained the C=O stretching mode at 1750 cm^{-1}. The nmr of XII indicated the presence of two acetoxy groups by showing two singlets of three protons each at 7.98 τ and 7.83 τ. The mass spectrum of XII contained a weak parent peak. This rearrangement was clearly analogous to the reaction of 2-methylpyridine *N*-oxide with acetic anhydride (4).

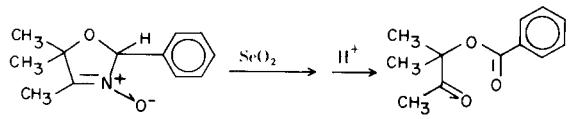
Treatment of I with selenium dioxide followed by hydrolysis with 1 *N* hydrochloric acid gave 2*H*-5,6-dihydro-2-(2-hydroxy-2-propyl)-5-keto-2,6,6-trimethyl-1,3-oxazine *N*-oxide (XIII).



XIII

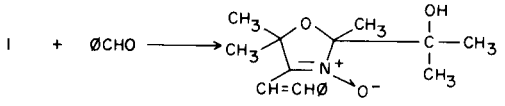
The oxidation and ring expansion of 2,4,4-trimethyl-Δ′-pyrroline *N*-oxide (5) was an analogous rearrangement reaction.

Treatment of 2-phenyl-4,5,5-trimethyl-3-oxazoline *N*-oxide (II) with selenium dioxide and hydrochloric acid gave 3-carbobenzoxy-3-methyl-2-butanone (XIV).



II XIV

It has been reported the pyrroline *N*-oxides undergo base catalyzed condensation with benzaldehyde and *p*-nitrobenzaldehyde to give monobenzylidene derivatives (6). Treatment of I with benzaldehyde in alcoholic potassium hydroxide gave 2-(2-hydroxy-2-propyl)-2,5,5-trimethyl-4-styryl-3-oxazoline *N*-oxide (XV).



XV

Due to the dipolar character of nitrones, many are known to undergo 1,3-cycloaddition reactions with olefins as reported by Huisgen (7,8) and Delpierre and Lamchen (9,10). However, styrene, ethyl acrylate, tetracyanoethylene, and acrylonitrile did not undergo cycloaddition to the nitrones. Dichloroketene, an extremely active diene, also failed to give any cycloaddition product.

EXPERIMENTAL

All infrared spectra were taken on a Perkin-Elmer Infracord 127 Spectrophotometer. Nuclear magnetic resonance spectra were taken on a Varian Associates A-60 Analytical NMR Spectrometer using tetramethylsilane as an internal standard. Mass spectra were taken on a Hitachi Perkin-Elmer RMU-6E Mass Spectrometer, and all gas chromatography was done with an Aerograph Gas Chromatograph Model A-90-P equipped with a 5′ x 1/4″ 10% SE-30 on 60-80 mesh Chromosorb G column with helium carrier gas at a flow rate of 60 cc/min. Melting points and boiling points were uncorrected.

3-Oxazolines.

The method described by Gaines and Hansen was used to prepare the 3-oxazoline compounds (2).

2-(2-Hydroxy-2-propyl)-2,4,5,5-tetramethyl-3-oxazoline *N*-Oxide (I).

A solution of 11.9 g. (0.05 mole) of 80% *m*-chloroperoxybenzoic acid in methylene chloride (75 ml.) was added dropwise with stirring to a solution of 9.3 g. (0.05 mole) of 2-(2-hydroxy-2-propyl)-2,4,5,5-tetramethyl-3-oxazoline in methylene chloride (25 ml.). The reaction mixture was refluxed with stirring for two hours after which the methylene chloride was removed *in vacuo*. The white solid residue was treated with 500 ml. of dry ether and stirred until solution was complete. Ammonia was then bubbled through the solution for 10 minutes and the ammonium salt of *m*-chlorobenzoic acid was filtered off using Celite filter aid. The ether solution was dried with magnesium sulfate and the ether was removed *in vacuo* to give a white solid which was recrystallized from *n*-hexane to give 9.6 g. (96%) of I, m.p. 77°; ir spectrum ν max 1630 (C=N), 1150 (N→O); nmr spectrum, τ (deuteriochloroform) 8.74 (6H, singlet), 8.50 (6H, singlet), 8.25 (3H, singlet), 7.93 (3H, singlet), 4.67 (1H, broad singlet); mass spectrum, m/e 201 (parent), 185 (p-16).

Anal. Calcd. for $C_{10}H_{19}NO_3$: C, 59.68; H, 9.52; N, 6.96. Found: C, 59.87; H, 9.57; N, 7.05.

2-Phenyl-4,5,5-trimethyl-3-oxazoline *N*-Oxide (II).

After treatment of 9.5 g. (0.05 mole) of 2-phenyl-4,5,5-trimethyl-3-oxazoline with *m*-chloroperoxybenzoic acid as described for I, and recrystallization from a 1:1 ether-hexane mixture, 8.4 g. (82%) of the white solid was obtained, m.p. 104°; ir spectrum, ν max 1635 (C=N), 1140 (N→O); nmr spectrum, τ (deuteriochloroform) 8.65 (3H, singlet), 8.40 (6H, singlet), 3.07 (1H, singlet), 2.55-1.90 (5H, multiplet); mass spectrum, m/e 205 (parent), 189 (p-16).

Anal. Calcd. for $C_{12}H_{15}NO_2$: C, 70.22. H, 7.37; N, 6.82. Found: C, 70.35; H, 7.53; N, 6.80.

2-Furyl-4,5,5-trimethyl-3-oxazoline *N*-Oxide (III).

After treatment of 9.0 g. (0.05 mole) of 2-furyl-4,5,5-trimethyl-3-oxazoline with *m*-chloroperoxybenzoic acid as described for I, and recrystallization from a 1:1 ether-hexane mixture, 8.1 g. (83%) of the white solid was obtained, m.p. 129°; ir spectrum, ν max 1655 (C=N), 1135 (N→O); nmr spectrum, τ (deuteriochloroform) 8.59 (3H, singlet), 8.33 (6H, singlet), 3.68 (1H, singlet), 2.65-2.30 (3H, multiplet); mass spectrum, m/e 195 (parent), 179 (p-16).

Anal. Calcd. for $C_{10}H_{13}NO_3$: C, 61.53; H, 6.71; N, 7.17. Found: C, 61.73; H, 6.89; N, 7.12.

2-(4-Chlorophenyl)-4,5,5-trimethyl-3-oxazoline *N*-Oxide (IV).

After treatment of 13.3 g. (0.05 mole) of 2-(4-chlorophenyl)-4,5,5-trimethyl-3-oxazoline with *m*-chloroperoxybenzoic acid as described for I, and recrystallization from benzene, 11.6 g. (92%) of the white solid was obtained, m.p. 264°; ir spectrum, ν max 1530 (C=N), 1100 (N→O); nmr spectrum, τ (deuteriochloroform) 8.61 (3H, singlet), 8.36 (6H, singlet), 3.48 (1H, singlet), 2.61-1.87 (4H, multiplet); mass spectrum, m/e 241 (parent), 225 (p-16).

Anal. Calcd. for $C_{12}H_{14}NO_2Cl$: C, 60.12; H, 5.89; N, 5.84. Found: C, 60.06; H, 5.87; N, 5.88.

2-(2-Hydroxyphenyl)-4,5,5-trimethyl-3-oxazoline *N*-Oxide (V).

After treatment of 11.0 g. (0.05 mole) of 2-(2-hydroxyphenyl)-4,5,5-trimethyl-3-oxazoline with *m*-chloroperoxybenzoic acid as described for I, and recrystallization from *n*-hexane, 10.5 g. (95%) of the white solid was obtained, m.p. 105°; ir spectrum, ν max 1620 (C=N), 1125 (N→O); nmr spectrum, τ (deuteriochloroform) 8.50 (3H, singlet), 8.26 (6H, singlet), 3.42 (1H, broad singlet), 3.14 (1H, broad singlet), 2.90-2.51 (4H, multiplet); mass spectrum, m/e 221 (parent), 205 (p-16).

Anal. Calcd. for $C_{12}H_{15}NO_3$: C, 65.14; H, 6.83; N, 6.33. Found: C, 65.31; H, 6.90; N, 6.28.

4,5-Dimethyl-5-ethyl-2-(4-methoxyphenyl)-3-oxazoline *N*-Oxide (VI).

After treatment of 12.4 g. (0.05 mole) of 4,5-dimethyl-5-ethyl-2-(4-methoxyphenyl)-3-oxazoline with *m*-chloroperoxybenzoic acid as described for I, and recrystallization from *n*-hexane, 11.6 g. (93%) of the white solid was obtained, m.p. 167°; ir spectrum ν max 1620 (C=N), 1125 (N→O); nmr spectrum, τ (deuteriochloroform) 8.89 (3H, triplet), 8.68 (3H, singlet), 8.38 (3H, singlet), 8.03 (2H, multiplet), 6.11 (3H, singlet), 3.17 (1H, singlet), 2.85-1.97 (4H, multiplet); mass spectrum, m/e 249 (parent), 233 (p-16).

Anal. Calcd. for $C_{14}H_{19}NO_3$: C, 67.44; H, 7.68; N, 5.61. Found: C, 67.54; H, 7.47; N, 5.55.

2-(4-Methoxyphenyl)-4,5,5-trimethyl-3-oxazoline *N*-Oxide (VII).

After treatment of 11.7 g. (0.05 mole) of 2-(4-methoxyphenyl)-4,5,5-trimethyl-3-oxazoline with *m*-chloroperoxybenzoic acid as described for I and recrystallization from *n*-hexane, 11.1 g. (95%) of the white solid was obtained, m.p. 181°; ir spectrum, ν max 1620 (C=N), 1140 (N→O); nmr spectrum, τ (deuteriochloroform) 8.68 (3H, singlet), 8.48 (6H, singlet), 6.15 (3H, singlet), 3.18 (1H, singlet), 2.98-2.00 (4H, multiplet); mass spectrum, m/e 235 (parent), 219 (p-16).

Anal. Calcd. for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.39; H, 7.31; N, 5.90.

5,5-Dimethyl-4-methylene-2-phenyl-2-oxazoline (VIII).

A mixture of 1.0 g. (5 mmoles) of 2-phenyl-4,5,5-trimethyl-3-oxazoline *N*-oxide II and 2.0 g. of magnesium sulfate in *m*-xylene (25 ml.) was refluxed for two hours. After filtration with the aid of Celite and removal of xylene *in vacuo* the residual yellow oil was distilled to give 0.9 g. (96%) of VIII, b.p. 68° (0.05 mm); ir spectrum, ν max 1600 (C=N), 1560 (C=C); nmr spectrum, τ (deuteriochloroform) 8.48 (6H, singlet, 5.50 (1H, singlet), 4.92 (1H, singlet), 2.55-1.90 (5H, multiplet); mass spectrum, m/e 187 (parent).

Anal. Calcd. for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41; N, 6.06. Found: C, 72.58; H, 7.49; N, 6.13.

5,5-Dimethyl-2-(4-methoxyphenyl)-4-methylene-2-oxazoline (IX).

After treatment of 1.0 g. (4.3 mmoles) of 2-(4-methoxyphenyl)-4,5,5-trimethyl-3-oxazoline *N*-oxide VII with magnesium sulfate in xylene as described for VIII, and distillation, 0.859 g. (92%) of IX was obtained, b.p. 81° (0.05 mm); ir spectrum, ν max 1610 (C=N), 1560 (C=C); nmr spectrum, τ (deuteriochloroform) 8.56 (6H, singlet), 6.15 (3H, singlet), 5.56 (1H, singlet), 4.98 (1H, singlet), 2.98-2.00 (4H, multiplet); mass spectrum, m/e 217 (parent).

Anal. Calcd. for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96; N, 6.45. Found: C, 71.96; H, 6.94; N, 6.32.

5-Ethyl-2-(4-methoxyphenyl)-5-methyl-4-methylene-2-oxazoline (X).

After treatment of 1.0 g. (4.0 mmoles) of 4,5-dimethyl-5-ethyl-2-(4-methoxyphenyl)-3-oxazoline *N*-oxide (VI) with magnesium sulfate in xylene as described for VIII, and distillation, 0.82 g. (89%) of X was obtained, b.p. 78° (0.05 mm); ir spectrum, ν max 1605 (C=N), 1580 (C=C); nmr spectrum, τ (deuteriochloroform) 8.90 (3H, triplet), 8.46 (3H, singlet), 8.03 (2H, multiplet), 6.11 (3H, singlet), 5.55 (1H, singlet), 4.97 (1H, singlet), 2.85-1.97 (4H, multiplet); mass spectrum, m/e 231 (parent).

Anal. Calcd. for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41; N, 6.06. Found: C, 72.58; H, 7.49; N, 6.13.

2-(2-Acetoxy-2-propyl)-2,4,5,5-tetramethyl-3-oxazoline *N*-oxide (XI).

A mixture of 2.05 g. (0.02 mole) of acetic anhydride and 4.0 g. (0.02 mole) of 2-(2-hydroxy-2-propyl)-2,4,5,5-tetramethyl-3-oxazoline *N*-oxide I was heated to 60° for 24 hours. Gas chromatography analysis of the mixture (column temperature, 160°), gave a 5:2, XI:I mixture from which XI was collected, ir spectrum ν max 1760 (C=O); nmr spectrum, τ (deuteriochloroform) 8.73 (3H, singlet), 8.61 (15H, singlet with shoulder), 7.85 (3H, singlet); mass spectrum, m/e 243 (parent).

Anal. Calcd. for $C_{12}H_{21}NO_4$: C, 59.24; H, 8.70; N, 5.76. Found: C, 58.99; H, 8.59; N, 5.61.

2-(2-Acetoxy-2-propyl)-2,5,5-trimethyl-4-acetoxymethyl-3-oxazoline (XII).

The crude reaction mixture from the preceding procedure was added to 2.05 g. (0.02 mole) of acetic anhydride and heated to 100° for 24 hours. The residual yellow oil was analyzed by gas chromatography (column temperature, 160°) and found to be a 2:1:1, XII:XI:I mixture from which XII was collected, ir spectrum ν max 1750 (C=O); nmr spectrum, τ (deuteriochloroform) 8.52 (9H, singlet with shoulder), 8.43 (5H, singlet), 7.98 (3H, singlet) 7.83 (3H, singlet), 5.10 (2H, singlet); mass spectrum, m/e 285 (parent).

Anal. Calcd. for $C_{14}H_{23}NO_5$: C, 58.93; H, 8.12; N, 4.91. Found: C, 58.87; H, 8.03; N, 4.96.

2*H*-5,6-Dihydro-2-(2-hydroxy-2-propyl)-5-keto-2,6,6-trimethyl-1,3-oxazine *N*-Oxide (XIII).

A solution of 2.01 g. (0.01 mole) of 2-(2-hydroxy-2-propyl)-2,4,5,5-tetramethyl-3-oxazoline *N*-oxide (I) and 1.11 g. (0.01 mole) of selenium dioxide in methanol (10 ml.) was refluxed for three hours. The deposited selenium was filtered off with the aid of Celite and the methanol was removed *in vacuo*. The red oily residue was treated with 1 *N* hydrochloric acid (10 ml.) and the solution was heated on a steam bath for 30 minutes, cooled and the deposited selenium was again removed. The filtrate was continuously extracted with ether for 12 hours. The ether solution was then passed through a short silica gel (20% water) column, dried with magnesium sulfate, and the ether was removed *in vacuo*. Upon addition of *n*-hexane the product precipitated and after recrystallization from a 1:1 ether-hexane mixture, 1.10 g. (52%) of

XIII was obtained, m.p. 148°; ir spectrum, ν max 1570, 1170; nmr spectrum, τ (deuteriochloroform) 8.70 (6H, singlet), 8.38 (6H, singlet), 8.20 (3H, singlet), 5.07 (1H, singlet), 1.87 (1H, singlet); mass spectrum, m/e 215 (parent), 172, 155, 103.

Anal. Calcd. for $C_{10}H_{17}NO_4$: C, 55.80; H, 7.96; N, 6.51. Found: C, 55.53; H, 7.84; N, 6.78.

3-Carbobenzoxy-3-methyl-2-butanone (XIV).

Upon treating 2.02 g. (0.01 mole) of 2-phenyl-4,5,5-trimethyl-3-oxazoline *N*-oxide (II) with selenium dioxide and dilute hydrochloric acid as previously described, 1.9 g. (92%) of XIV was obtained, b.p. 73° (0.05 mm); ir spectrum, ν max 1710, 1280; nmr spectrum, τ (deuteriochloroform) 8.40 (6H, singlet), 7.83 (3H, singlet), 2.55-1.85 (5H, multiplet); mass spectrum, m/e 206 (parent), 163, 105.

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.87; H, 6.85. Found: C, 69.88; H, 6.83.

The 2,4-dinitrophenylhydrazone of XIV was prepared, m.p. 157°.

Anal. Calcd. for $C_{18}H_{18}N_3O_6$: C, 55.95; H, 4.70; N, 14.50. Found: C, 56.08; H, 4.53; N, 14.41.

2-(2-Hydroxy-2-propyl)-2,5,5-trimethyl-4-styryl-3-oxazoline *N*-Oxide (XV).

A mixture of alcoholic potassium hydroxide (10 ml.), 1.06 g. (0.01 mole) of benzaldehyde, and 2.01 g. (0.01 mole) of 2-(2-hydroxy-2-propyl)-2,4,5,5-tetramethyl-3-oxazoline *N*-oxide (I) was refluxed for 30 minutes, cooled, and then was poured into water (100 ml.). The yellow precipitate was collected and was recrystallized from ligroin to give 1.69 g. (60%) of XV, m.p. 94°; ir spectrum, ν max 1620 (C=N), 1560 (C=C), 1170 (N→O); nmr spectrum, τ (deuteriochloroform) 8.68 (6H, singlet), 8.35 (6H, singlet), 8.18 (3H, singlet), 5.05 (1H, singlet), 4.89 (1H, doublet), 3.40 (1H, doublet), 3.0-2.6 (5H, multiplet); mass spectrum, m/e 289 (parent), 214, 188, 172.

Anal. Calcd. for $C_{17}H_{23}NO_3$: C, 70.56; H, 8.01; N, 4.84. Found: C, 70.67; H, 8.16; N, 5.01.

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