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REGIOSELECTIVE SYNTHESIS OF 4-ACETYL- AND 5-ACETYL-3-METHYLISOXAZOLE: THEIR CONVERSION INTO SILYL- AND METHYL ENOL ETHERS

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Abstract: Acetonitrile oxide reacts regioselectively with 3-buten-2-one and (*E*)-4-methoxy-3-buten-2-one to give 5-acetyl- **2** and 4-acetyl-3-methylisoxazole **3**, respectively. Treatment of ketones **2** and **3** with trimethylsilyl trifluoromethanesulfonate gave the silyl enol ethers **4** and **5**, whereas the methyl enol ethers **8** and **9** were obtained *via* elimination of methanol from the corresponding dimethyl ketals.

The 1,3-dipolar cycloaddition of nitrile oxides to substituted alkenes represents the most convenient method for the synthesis of five membered heterocyclic rings as isoxazoles or their dihydro derivatives.[1] We wish to report here on the different regioselectivity observed in the reaction of acetonitrile oxide with 3-buten-2-one (methyl vinyl ketone) and (*E*)-4-methoxy-3-buten-2-one (methyl *trans*-2-methoxyvinyl ketone) and on their conversion into enol ethers.

Thus, reaction of acetonitrile oxide with methyl vinyl ketone gave rise[2] almost exclusively to the primary cycloadduct **1b**, the 4-substituted regioisomer **1a** being present only in traces (4%) as determined by a gas-chromatographic analysis and by the ^{1}H NMR spectrum of the crude reaction mixture. This regiochemistry, which seems to be governed primarily by the

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LUMO dipole-HOMO dipolarophile interaction,[1] is also in accord with other reactivity data in the field of 1,3-dipolar cycloaddition with vinyl carbonyl compounds.[3] Subsequent treatment of the isoxazoline **1b** with active γ-manganese dioxide in refluxing benzene[4] led to the ketone **2** in good yield.

However, when the same cycloaddition reaction is carried out employing the captodative (*E*)-4-methoxy-3-buten-2-one, the opposite regiochemistry was observed and the 4-substituted isoxazole **3** was obtained as the sole reaction product in very good yield (88%).

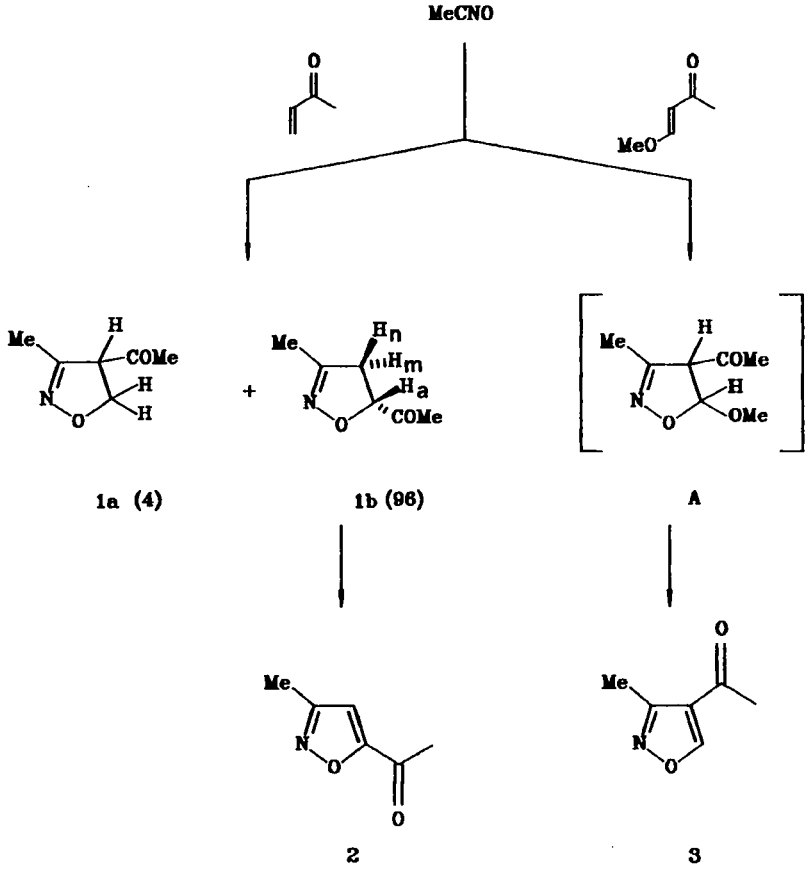


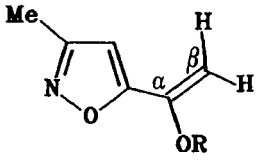
Table 1
^{1}H NMR ($CDCl_3$, 200 MHz) chemical shifts (δ, ppm) of compounds **1-9**

Comp.[a]	H-4	H-5	3Me	COMe	CH_2[b]	Cα-Me	Others
1b[c]	3.15 (1H, H-m, $^2J_{m,n}$ = 17.0, $^3J_{m,a}$ = 7.0, $^4J_{m,x_3}$ = 1.1), 3.08 (1H, H-n, $^2J_{n,m}$ = 17.0, $^3J_{n,a}$ = 10.7, $^4J_{n,x_3}$ = 1.0,)	4.80 (H-a, $^3J_{a,n}$ = 10.7, $^3J_{a,m}$ = 7.0)	1.98 (3H, H-x_3, $^4J_{x_3,m}$ = 1.1, $^4J_{x_3,n}$ = 1.0)	2.27 (s)	-	-	-
2	6.74 (q, $^4J_{4,3Me}$ = 0.3)	-	2.38 (d, $^4J_{3Me,4}$ = 0.3)	2.60 (s)	-	-	-
3	-	8.85 (q, $^5J_{5,3Me}$ = 0.6)	2.51(d, $^5J_{3Me,5}$ = 0.6)	2.48 (s)	-	-	-
4	6.11 (s)	-	2.30 (s)	-	5.16 (1H, $^2J_{a,b}$ = 2.0) 4.61 (1H, $^2J_{a,b}$ = 2.0)	-	0.27 (s, 3xMe)
5	-	8.36 (q, $^5J_{5,3Me}$ = 0.6)	2.38 (d, $^5J_{3Me,5}$ = 0.6)	-	4.56 (1H, $^2J_{a,b}$ = 2.0) 4.41 (1H, $^2J_{a,b}$ = 2.0)	-	0.26 (s, 3xMe)
6	6.14 (s)	-	2.30 (s)	-	-	1.64 (s)	3.21 (s, 2xOMe)
7	-	8.28 (q, $^5J_{5,3Me}$ = 0.6)	2.32 (d, $^5J_{3Me,5}$ = 0.6)	-	-	1.54 (s)	3.16 (s, 2xOMe)
8	6.19 (s)	-	2.30 (s)	-	5.00 (1H, $^2J_{a,b}$ = 3.1) 4.46 (1H, $^2J_{a,b}$ = 3.1)	-	3.72 (s, OMe)
9	-	8.43 (q, $^5J_{5,3Me}$ = 0.6)	2.39 (d, $^5J_{3Me,5}$ = 0.6)	-	4.38 (1H, $^2J_{a,b}$ = 3.0) 4.27 (1H, $^2J_{a,b}$ = 3.0)	-	3.68 (s, OMe)

a) Multiplicity (s = singlet, d = doublet, q = quartet), $J_{H,H}$ (Hz). b) AB system. c) Chemical shifts and coupling constants from the simulated spectrum (LAOCN 3).

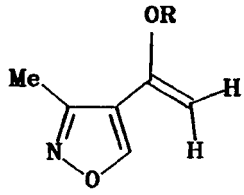
The observed regioselectivity can be easily predicted from FMO considerations on the reacting systems[5] and considering the high preference of the methoxy substituent for the 5 position of the isoxazoline ring,[1,7] analogously to what observed for the amino[1] or methylthio[6] groups. The primary cycloadduct **A** could not even be observed in the reaction mixture, elimination of methanol giving rise to the aromatic 4-acetyl isomer **3** as the only isolated compound.

Both the acetyl derivatives **2** and **3** were fully characterized by spectroscopic methods; in particular, the ^{1}H NMR signals of the 3-Me and COMe groups can be easily distinguished owing to the small coupling (Table 1) between the 3-Me and H-4 or H-5 which can be recognized also in a long-range optimized COSY experiment.[8]



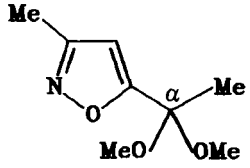
4 R = $SiMe_3$

8 R = Me



5 R = $SiMe_3$

9 R = Me



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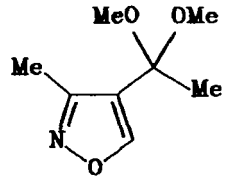

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Table 2

^{13}C NMR ($CDCl_3$, 75 MHz) chemical shifts (δ,ppm) of selected compounds

Comp.[a]	C-3	C-4	C-5	3Me	CO	Me	C-α	C-β	$SiMe_3$	OMe
1b	155.46(m)	40.70(tdq)[b]	83.46(dm)	12.78(q)	207.96(qdd)[c]	26.35(q)	-	-	-	-
2	160.62(dq)[d]	107.78(dq)	166.43(d)	11.43(q)	187.04(q)	27.20(q)	-	-	-	-
3	158.37(dq)[d]	120.65(dm)	162.28(d)	11.07(q)	190.96(q)	28.95(q)	-	-	-	-
4	160.01(dq)[d]	101.84(dq)	167.66(ddd)[e]	11.42(q)	-	-	145.16(dd)[f]	95.88(dd)	-0.08(qsep)	-
5	156.39(dq)[d]	119.32(m)	156.07(d)	11.54(q)	-	-	147.43(dd)[f]	92.66(dd)[f]	-0.12(qsep)	-
8	160.00(dq)[d]	101.41(dq)	165.93(ddd)[e]	11.42(q)	-	-	150.47(qdd)[c]	86.25(dd)	-	55.06(q)
9	156.58(dq)	117.61(m)	156.00(d)	11.51(q)	-	-	152.65(qdd)[c]	83.64(dd)	-	54.76(q)

a) Multiplicity in the ^1H-coupled spectra (d = doublet, t = triplet, q = quartet, sep = septuplet, m = multiplet).
b) Appears as triplet of quintets.
c) Appears as sestuplet.
d) Appears as quintet.
e) Appears as triplet of doublets.
f) Appears as triplet.

Table 3

$^{n}J_{C,H}$ (Hz) of selected compounds

Comp.	C-3	C-4	C-5	3-Me	Others
1b	m	$^{1}J_{C4\text{-}H4}$ = 136.2 $^{2}J_{C4\text{-}H5}$ = 2.8 $^{3}J_{C4\text{-}3Me}$ = 2.8	m	$^{1}J_{3Me}$ = 129.7	$^{2}J_{CO\text{-}Me}$ = 6.3, $^{3}J_{CO\text{-}Ha,b}$ =6.3, $^{1}J_{Me}$ = 128.6
2	$^{2}J_{C3\text{-}3Me}$ = 6.5 $^{2}J_{C3\text{-}H4}$ = 6.5	$^{1}J_{C4\text{-}H4}$ = 183.5 $^{3}J_{C4\text{-}3Me}$ = 3.1	$^{2}J_{C5\text{-}H4}$ = 9.0	$^{1}J_{3Me}$ = 129.8	$^{2}J_{CO\text{-}Me}$ = 6.4, $^{1}J_{Me}$ = 129.0
3	$^{2}J_{C3\text{-}3Me}$ = 7.2 $^{3}J_{C3\text{-}H5}$ = 7.2	m	$^{1}J_{C5\text{-}H5}$ = 200.3	$^{1}J_{3Me}$ = 130.8	$^{2}J_{CO\text{-}Me}$ = 5.9, $^{1}J_{Me}$ = 127.9
4	$^{2}J_{C3\text{-}3Me}$ = 6.5 $^{2}J_{C3\text{-}H4}$ = 6.5	$^{1}J_{C4\text{-}H4}$ = 181.8 $^{3}J_{C4\text{-}3Me}$ = 3.2	$^{2}J_{C5\text{-}H4}$ = 8.5 $^{3}J_{C5\text{-}Hb}$ = 8.5 $^{3}J_{C5\text{-}Ha}$ = 3.3	$^{1}J_{3Me}$ = 129.2	$^{2}J_{C\alpha\text{-}Ha,b}$ = 4.0, $^{1}J_{C\beta\text{-}Ha,b}$ = 163.0 and 159.8, $^{1}J_{Me}$ = 119.0, $^{3}J_{Me\text{-}Me}$ = 1.9
5	$^{2}J_{C3\text{-}3Me}$ = 6.8 $^{3}J_{C3\text{-}H5}$ = 6.8	m	$^{1}J_{C5\text{-}H5}$ = 202.4	$^{1}J_{3Me}$ = 129.2	$^{2}J_{C\alpha\text{-}Ha,b}$ = 4.5, $^{1}J_{C\beta\text{-}Ha,b}$ = 158.3, $^{1}J_{Me}$ = 119.0, $^{3}J_{Me\text{-}Me}$ = 1.6
8	$^{2}J_{C3\text{-}3Me}$ = 6.7 $^{2}J_{C3\text{-}H4}$ = 6.7	$^{1}J_{C4\text{-}H4}$ = 182.3 $^{3}J_{C4\text{-}3Me}$ = 3.1	$^{3}J_{C5\text{-}H4}$ = 8.7 $^{3}J_{C5\text{-}Hb}$ = 8.7 $^{3}J_{C5\text{-}Ha}$ = 3.8	$^{1}J_{3Me}$ = 129.3	$^{3}J_{C\alpha\text{-}OMe}$ = 4.3, $^{2}J_{C\alpha\text{-}Ha,b}$ = 4.3, $^{1}J_{C\beta\text{-}Ha,b}$ = 164.3 and 160.6, $^{1}J_{OMe}$ = 144.5
9	$^{2}J_{C3\text{-}3Me}$ = 6.8 $^{3}J_{C3\text{-}H5}$ = 5.7	m	$^{1}J_{C5\text{-}H5}$ = 202.6	$^{1}J_{3Me}$ = 129.7	$^{3}J_{C\alpha\text{-}OMe}$ = 4.4, $^{2}J_{C\alpha\text{-}Ha,b}$ = 4.4, $^{1}J_{C\beta\text{-}Ha,b}$ = 161.2 and 159.1, $^{1}J_{OMe}$ = 144.1

In the course of our work we needed the enol ethers derived from the heterocyclic ketones **2** and **3**. Thus, the latter compounds were gently refluxed with trimethylsilyl trifluoromethanesulfonate (trimethylsilyl triflate) and triethylamine in dry benzene[9] to afford the desired silyl derivatives **4** or **5**. The less sterically hindered methyl enol ethers **8** and **9** can be obtained through acid-catalyzed elimination of methanol[10] from the corresponding ketals **6** and **7**.

^{1}H And ^{13}C NMR data of the compounds are reported in Tables 1,2 and 3. In particular, the $AMNX_3$ spin system of the isoxazoline **1b** was resolved by simulation (LAOCN 3)[11] thus obtaining a value of 17.0 Hz for the geminal coupling constant of the 4-CH_2 group which is in excellent agreement with those previously reported (16.8-17.3 Hz) for similar compounds.[12]

EXPERIMENTAL

All melting points were determined on a Büchi melting point apparatus and are uncorrected. Carbon-13 and proton NMR spectra were recorded on a Varian VXR-300 or a Varian Gemini-200 instrument in the Fourier transform mode. All carbon spectra were recorded at 25 ± 0.5 °C for 0.5 M solutions in anhydrous $CDCl_3$, proton coupled spectra were obtained in the 'gated decoupling' mode. Chemical shifts are reported in ppm high frequency from TMS as secondary reference standard and coupling constants in Hz. Mass spectra were registered with a Carlo Erba QMD 1000 instrument at 70 eV. IR spectra were recorded with a Perkin Elmer 881 spectrophotometer in KBr pellets. Silica gel plates (Merck F_{254}) and silica gel 60 (Merck 230-400 mesh) were used for analytical tlc and for flash chromatographies, respectively. Solvents were removed under reduced pressure. Acetonitrile oxide was prepared *in situ* by the method of Mukaiyama.[13] (*E*)-4-Methoxy-3-buten-2-one and 3-buten-2-one are commercially available (Aldrich Chemical Co.) and were used without further purification.

5-Acetyl-3-methyl-4,5-dihydroisoxazole, 1b

A solution of nitroethane (7.2 g, 96 mmol) and triethylamine (20 drops) in dry benzene (20 ml) was added dropwise to a solution of phenyl isocyanate (20.7 g, 174 mmol) and 3-buten-2-one (6.7 g, 95 mmol) in dry benzene (35 ml). After stirring for 1 h, the reaction mixture was refluxed for an additional hour, cooled and checked. The ^{1}H NMR of a neat aliquot showed the presence of compounds **1a** and **1b** in the ratio 4:96, respectively. The solid was filtered off, and the filtrate was concentrated to give a yellow oil which was distilled to afford pure compound **1b** (9.1 g, 75% yield): b.p. 57-58 °C/0.2 mmHg (lit.[2] 56-57 °C/0.8 mmHg). MS, *m/z* (%): 127 (M^+, 10), 84 (M^+-43, 88), 56 (M^+-43-28, 100).

5-Acetyl-3-methylisoxazole, 2

Compound **1b** (2.0 g, 15.7 mmol) in dry benzene (50 ml) and active γ-manganese dioxide (5.0 g) were refluxed for 3 h, while the water formed was removed by means of a Dean-Stark trap. The end of the reaction was monitored by ^{1}H NMR. The solid was filtered through Celite and washed with the same solvent. Evaporation of the filtrate left compound **2** (1.5 g, 76%) which was purified by sublimation at 40 °C/20 mmHg: m.p. 73-74 °C (lit. [14] 75 °C, lit. [15] 71-72 °C). MS, *m/z* (%): 125 (M^+, 100), 110 (M^+-15, 32), 82 (M^+-43, 30). IR (KBr, cm^{-1}): 3120, 1695 (CO), and 1590.

4-Acetyl-3-methylisoxazole, 3

A solution of nitroethane (2.5 g, 33.5 mmol) and triethylamine (15 drops) in dry benzene (15 ml) was added dropwise to a solution of 4-chlorophenyl isocyanate (8.6 g, 56 mmol) and *trans*-4-methoxy-3-buten-2-one (3.0 g, 30 mmol) in dry benzene (25 ml). The reaction mixture was stirred for 1 h, then refluxed for an additional hour, cooled and checked. The ^{1}H NMR of a neat aliquot showed the presence of starting material. Thus, operating as above, 4-chlorophenyl isocyanate (6.2 g, 41 mmol), nitroethane (1 ml, 9.8 mmol) and 5 drops of triethylamine were added to the reaction mixture. The solid was filtered off and the filtrate was concentrated to give a yellow oil, which was distilled to give compound **3** (3.3 g, 88%

yield): b.p. 110 °C/18 mmHg; m.p. 46.5-47.5 °C (after sublimation at 25 °C/20 mmHg). MS, *m/z* (%): 125 (M^+, 44), 110 (M^+-15, 54), 82 (M^+-43, 100), 43 (52). IR (KBr, cm^{-1}): 3100, 1685 (CO), and 1585. Anal. Calcd. for $C_6H_7NO_2$: C, 57.59; H, 5.64; N, 11.19. Found: C, 57.45; H, 5.52; N, 11.06.

5[(1-Trimethylsiloxy)vinyl]-3-methylisoxazole, 4

A solution of trimethylsilyl trifluoromethanesulfonate (2.54 g, 11.4 mmol) in dry benzene (3 ml) was added dropwise to a previously cooled (0 °C) solution of compound **2** (1.3 g, 10.4 mmol) and triethylamine (1.16 g, 11.4 mmol) in dry benzene (15 ml). The reaction mixture was refluxed for 2 h and then extracted with benzene (4 x 20 ml). The extracts were dried over sodium sulfate and evaporated to yield a brownish oil which was distilled to give compound **4** (1.9 g, 93%): b.p. 62 °C/0.15 mmHg. MS, *m/z* (%): 197 (M^+, 18), 182 (M^+-15, 100), 167 (M^+-30, 13), 152 (M^+-45, 48), 75 (19), 73 (52). Anal. Calcd. for $C_9H_{15}NO_2Si$: C, 54.79; H, 7.66; N, 7.10. Found: C, 54.68; H, 7.53; N, 6.94.

4[(1-Trimethylsiloxy)vinyl]-3-methylisoxazole, 5

A solution of trimethylsilyl trifluoromethanesulfonate (0.978 g, 4.4 mmol) in dry benzene (1 ml) was added dropwise to a previously cooled (0 °C) solution of compound **3** (0.5 g, 4.0 mmol) and triethylamine (0.445 g, 4.4 mmol) in dry benzene (5 ml). The reaction mixture was refluxed for 2 h and then extracted with benzene (4 x 20 ml). The extracts were dried over sodium sulfate and evaporated to yield a brownish oil which was distilled to give compound **5** (0.528 g, 67%): b.p. 84-85 °C/0.7 mmHg. MS, *m/z* (%): 197 (M^+, 25), 182 (M^+-15, 34), 167 (M^+-30, 16), 152 (M^+-45, 10), 141 (16), 140 (18), 75 (100), 73 (91). Anal. Calcd. for $C_9H_{15}NO_2Si$: C, 54.79; H, 7.66; N, 7.10. Found: C, 54.55; H, 7.62; N, 7.06.

5[(1,1-Dimethoxy)ethyl]-3-methylisoxazole, 6

A solution of compound **2** (0.75 g, 6 mmol), trimethyl orthoformate (1.26 g, 12 mmol) and *p*-toluenesulfonic acid (0.2 g) in methanol (9 ml) was heated at 120 °C for 5 h, poured into a

saturated solution of sodium hydrogen carbonate (30 ml) and extracted with chloroform (4x10 ml). The organic solution was washed with water (3 x 10 ml) and dried over sodium sulfate. Removal of the solvent left compound **6** as a pale yellow oil (1.0 g, 97%). MS, *m/z* (%): 171 (M^+, 0.6), 156 (M^+-15, 31), 140 (M^+-31, 100), 82 (12); ^{13}C NMR ($CDCl_3$) δ 171.22 (C-5), 159.48 (C-3), 103.67 (C-4, $^1J_{C4-H4}$ = 182.4 Hz), 98.42 (C-α), 49.21 (2 x OMe), 22.78 (Cα-*Me*), 11.42 (3-Me). Anal. Calcd. for $C_8H_{13}NO_3$: C, 56.13; H, 7.65; N, 8.18. Found: C, 56.18; H, 7.54; N, 8.11.

4[(1,1-Dimethoxy)ethyl]-3-methylisoxazole, 7

A solution of compound **3** (3.2 g, 25.6 mmol), trimethyl orthoformate (2.7 g, 25.6 mmol) and *p*-toluenesulfonic acid (0.04 g) in methanol (36 ml) was heated at 40 °C for 2 h, poured into a saturated solution of sodium hydrogen carbonate (30 ml) and extracted with chloroform (4 x 15 ml). The organic solution was washed with water (3 x 10 ml) and dried over sodium sulfate. Removal of the solvent left compound **7** as a colorless oil (4.1 g, 94%). MS, *m/z* (%): 171 (M^+, 0.5), 156 (M^+-15, 43), 140 (M^+-31, 100), 108 (89), 82 (25); ^{13}C NMR ($CDCl_3$) δ 157.45 (C-5, $^1J_{C5-H5}$ = 203.5 Hz), 156.78 (C-3), 121.56 (C-4), 98.41 (C-α), 48.58 (2 x OMe), 23.98 (Cα-*Me*), 10.28 (3-Me). Anal. Calcd. for $C_8H_{13}NO_3$: C, 56.13; H, 7.65; N, 8.18. Found: C, 56.05; H, 7.60; N, 8.09.

5[(1-Methoxy)vinyl]-3-methylisoxazole, 8

Phosphorus pentoxide (4.0 g, 27.5 mmol) was added under vigorous mechanical stirring to a solution of compound **6** (1.3 g, 7.6 mmol) in pyridine (10 ml). The mixture was refluxed for 40 h and then exhaustively extracted with chloroform. Pure compound **8** (0.528 g, 50%) was obtained by flash-chromatography (ethyl acetate : petroleum ether b.p. 40-70 °C, 1:5 v/v as eluant). MS, *m/z* (%): 139 (M^+, 100), 109 (3), 98 (4), 82 (80), 68 (29), 57 (22), 42 (41). Anal. Calcd. for $C_7H_9NO_2$: C, 60.42; H, 6.52; N, 10.07. Found: C, 60.48; H, 6.70; N, 9.90.

4[(1-Methoxy)vinyl]-3-methylisoxazole, 9

Phosphorus pentoxide (1.7 g, 11.7 mmol) was added under vigorous mechanical stirring to a solution of compound **7** (1.0 g, 5.8 mmol) in pyridine (4 ml). The mixture was refluxed for 3 h and then exhaustively extracted with chloroform. Pure compound **9** (0.467g, 59%) was obtained by flash-chromatography (ethyl acetate-petroleum ether b.p. 40-70 °C, 1:5 v/v as eluant). MS, *m/z* (%): 139 (M^+, 93), 110 (24), 82 (53), 68 (73), 42 (100). Anal. Calcd. for $C_7H_9NO_2$: C, 60.42; H, 6.52; N, 10.07. Found: C, 60.35; H, 6.61; N, 9.92.

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