Synthesis of 2-Imino-4-thiazolines, 2-Imino-4-alkoxythiazolidines, Thiazoles and 4-Imidazolin-2-ones from α-Halomethyl Ketimines

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A variety of heterocycles, including 3,4-disubstituted-2-imino-4-thiazolines, 3,4-disubstituted-4-methoxy-2-iminothiazolidines, 2,4-disubstituted-thiazoles, 2-amino-4-substituted-thiazoles and 1,5-disubstituted-4-imidazolin-2-ones, were synthesized from α-chloromethyl and α-bromomethyl ketimines by condensation with potassium thiocyanate, thiourea, ammonium thiocyanate and potassium cyanate.

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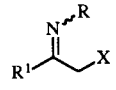
Introduction.

α-Halomethyl ketimines **1**, *i.e.* imines derived from 1-halo-2-alkanones, became only recently available as a convenient source of a 2-oxoalkyl unit [1]. These new reactive bielectrophilic reagents were found to react conveniently with iodide, alkoxides, thiolates and secondary amines to give the substitution products [1]. However, cyanide converted α-halomethyl ketimines into α-cyanoaziridines while primary amines afforded initially nucleophilic substitution, but the resulting α-(*N*-alkylamino)ketimines oxidized spontaneously in the air to give α-diimines [1]. The various nucleophilic interactions with the halogenated carbon and the imino carbon of α-halomethyl ketimines allow to predict

Chart 1



1 X = Cl, Br

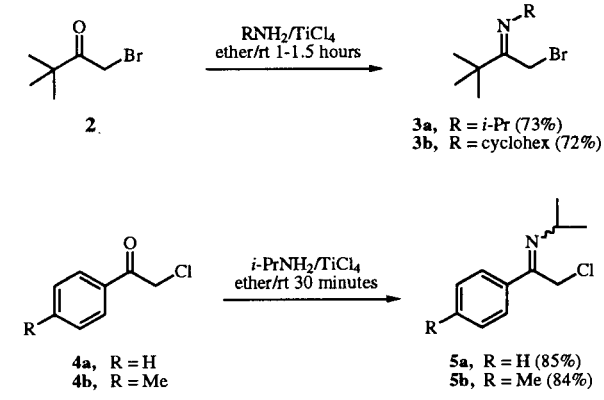
useful condensation reactions with ambident nucleophiles, *e.g.* thiocyanate, cyanate, thiourea, *etc.* A double interaction with both electrophilic centers of α-halomethyl ketimines creates the possibility for the construction of heterocyclic compounds. In this report, attention is paid to reactions of α-halomethyl ketimines with potassium and ammonium thiocyanate, thiourea, thioacetamide and potassium cyanate because the target heterocycles have potential physiological activities in various domains such as in agrochemistry and the pharmaceutical field.

Results and Discussion.

α-Bromomethyl and α-chloromethyl ketimines **3** and **5** were synthesized by condensation of the appropriate α-bromomethyl or α-chloromethyl ketone **2** and **4** with primary amines in diethyl ether in the presence of stoechiometric amounts of titanium(IV) chloride (Scheme 1) [1].

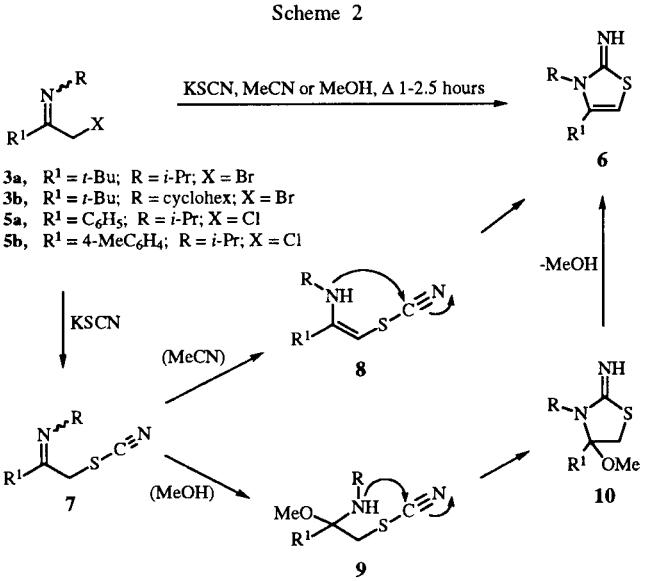
The ambident nucleophilic potassium thiocyanate reacted with α-halomethyl ketimines **3** and **5** to give the substitution

Scheme 1

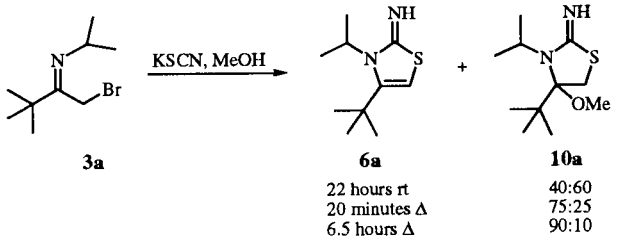


product **7** as an intermediate, which underwent intramolecular nucleophilic addition (*via* enamine **8**) to provide 3-alkyl-2-imino-4-thiazolines **6** in 60-77% yield (Scheme 2, Table I). The synthesis of these heterocycles proceeded in acetonitrile as well as in methanol. Using methanol as solvent, the formation of 3,4-dialkyl-2-imino-4-methoxythiazo-

Scheme 2



Scheme 3



lidines **10** was also observed. The latter adduct of methanol disappeared gradually upon increasing the reaction temperature and the reaction time. For example, α-bromomethyl ketimine **3a** reacted with potassium thiocyanate in methanol at room temperature for 22 hours to afford 4-*t*-butyl-2-imino-3-isopropyl-4-methoxythiazolidine **10a** and 4-*t*-butyl-2-imino-4-thiazoline **6a** in a 60:40 ratio, respectively. Under reflux conditions the ratios changed from 25:75 (reflux 20 minutes) to 10:90 (reflux 6.5 hours), respectively (Scheme 3). These results are indicative of the intermediacy of an adduct **9** which cyclizes and subsequently expels the elements of methanol (Scheme 2).

Table I gives a compilation of the conversion of α-halomethyl ketimines **3** and **5** into 3,4-disubstituted-2-imino-4-thiazolines **6**.

Table I

Synthesis of 3,4-Disubstituted-2-imino-4-thiazolines **6** from α-Halomethyl Ketimines **3** and **5**

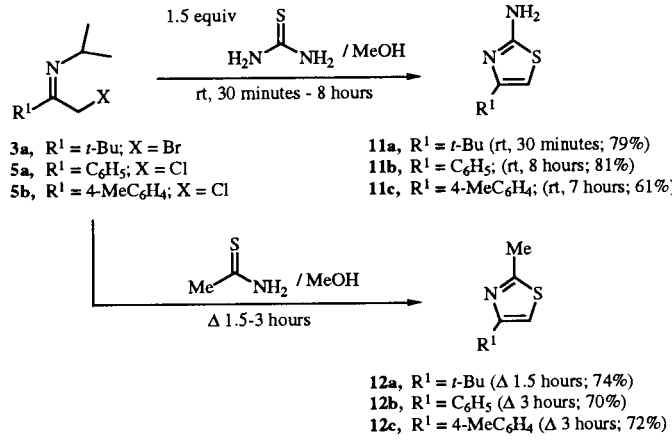
Starting Material	R^1	R	X [a]	Reaction Conditions [b]	Yield
3a	*t*-Bu	*i*-Pr	Br	70°/2.5 hours	**6a**: 60%
3b	*t*-Bu	cyclohex	Br	60°/1 hour	**6b**: 77%
5a	C_6H_5	*i*-Pr	Cl	70°/1.3 hours	**6c**: 75%
5b	4-MeC_6H_4	*i*-Pr	Cl	70°/2.5 hours	**6d**: 62%

[a] Halogen atom in the starting α-halomethyl ketimine. [b] Acetonitrile (1.5 molar equivalents of KSCN, 10% w/v).

Based on the above results, it is most probable that the substitution product **7** gives ring closure *via* the enamine form **8** [2], while in a nucleophilic solvent (*e.g.* methanol), adduct formation takes place, the resulting adduct **9** affording ring closure similarly.

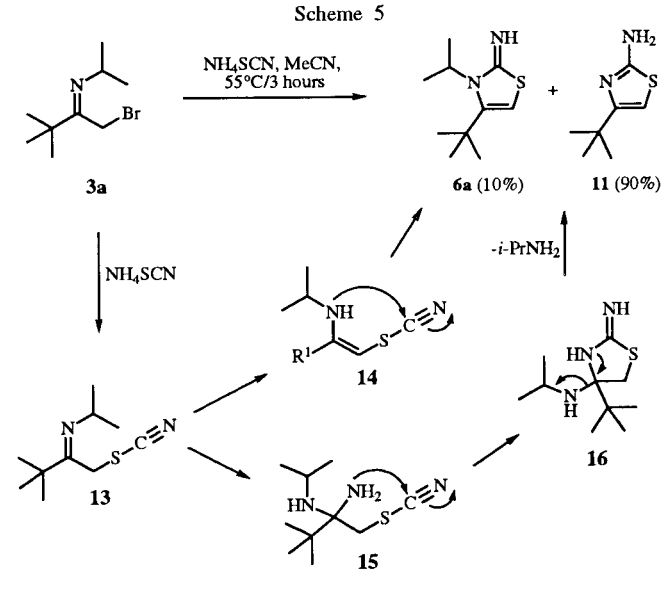
Other ambident nucleophiles such as thiourea and thioacetamide condensed with α-halomethyl ketimines **3a** and **5** in methanol to afford 2-aminothiazoles **11** and 2-methylthiazoles **12**, respectively (Scheme 4). The thiazoles **11a** and **12a** are likewise obtained from the corresponding α-bromoketone, *i.e.* 1-bromo-3,3-dimethyl-2-butanone, according to the classical Hantzsch thiazole synthesis [3,4]. As the *N*-isopropyl moiety is lost during the condensation of the α-haloketimines **3a** and **5**, this synthetic procedure for thiazoles is less attractive.

Scheme 4



However, the reaction of α-bromoketimine **3a** with ammonium thiocyanate in acetonitrile yielded 2-amino-4-*t*-butylthiazole **11a** as the major reaction product (90%), accompanied by 10% of 4-*t*-butyl-3-isopropyl-2-imino-4-thiazoline **6a** (Scheme 5). The initial substitution product **13** underwent competitive cyclization to 2-imino-4-thiazoline **6a** or 2-aminothiazole **11a**, the latter according to

Scheme 5

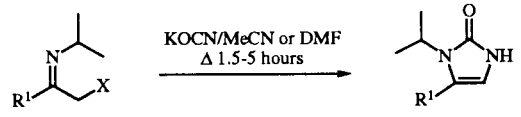


exchange of an intermediate isopropylamino moiety for an amino moiety. While the intermediate substitution product **13** can cyclize *via* the enamine **14**, the addition of ammonia across the imino bond of **13** forms an adduct which is able to cyclize to **16** after which it looses isopropylamine to give the major heterocycle **11a**.

In contrast to the foregoing results, the condensation of ketimines **3a** and **5** with potassium cyanate took a different course in that it resulted in the formation of 4-imidazolin-2-ones **17**. The reaction of α-bromomethyl ketimine

3a with 1.5 molar equivalents of potassium cyanate in acetonitrile under reflux for 1.5 hours afforded 5-*t*-butyl-1-isopropyl-4-imidazolin-2-one **17a** in 75% yield (Scheme 6). α-Chloromethyl ketimines **5** reacted similarly with potassium cyanate (1.5 equivalents) to give 4-imidazolin-2-ones **17b,c**. However, this reaction required a prolonged reaction time and a higher reaction temperature (5 hours reflux in DMF). The structure of the

Scheme 6



3a, R^1 = *t*-Bu; X = Br
5a, R^1 = C_6H_5; X = Cl
5b, R^1 = 4-MeC_6H_4; X = Cl

17a, R^1 = *t*-Bu (MeCN, Δ 1.5 hours; 75%)
17b, R^1 = C_6H_5 (DMF, Δ 5 hours; 60%)
17c, R^1 = 4-MeC_6H_4; (DMF, Δ 5 hours; 63%)

4-imidazolin-2-ones **17** was established by spectroscopic methods and by comparison of ^{13}C nmr data of known analogues. These results demonstrate that halomethyl ketimines can be used for the construction of these five membered heterocycles. It should be stressed that these syntheses of heterocycles are usually highly dependent on the substitution pattern in the starting material and that by no means general syntheses of such heterocycles exist. The present results show that 2-imino-4-thiazolines and 4-imidazolin-2-ones with aliphatic or aromatic substituents at the 4-position and no substituent at the 5-position are accessible.

In conclusion, α-halomethyl ketimines are suitable building blocks for the conversion into a variety of heterocycles with potential physiological activities. For instance, 2-imino-4-thiazolines have been reported to display insecticidal [5], schistosomicidal [6] and plant growth regulating [7] activity. On the other hand, 4-imidazolin-2-ones are known for their pharmaceutical and agrochemical properties. Activities of the former are situated in the field of herbicides [8] and antibacterials [9], while the latter properties refer to anticonvulsant [10], cardiotonic [11] and analgesic [12] activity.

EXPERIMENTAL

Ir spectra were recorded with a Perkin Elmer model 1310 spectrophotometer. The ^1H nmr spectra were measured with a Varian T-60, a Jeol PMX60 nmr spectrometer (60 MHz) or a Jeol JNM EX270 nmr spectrometer (270 MHz), while ^{13}C nmr spectra were recorded with a Varian FT-80 nmr spectrometer (20 MHz) or a Jeol JNM EX270 nmr spectrometer (68 MHz). Mass spectra were obtained with a Varian Matt 112 mass spectrometer (70 eV) using a direct inlet system or by using a gc-ms coupling (capillary column).

α-Bromomethyl ketimines **3a,b** and α-chloromethyl ketimines **5** were synthesized by condensation of the corresponding α-haloketones **2** and **4** with primary amines in diethyl ether in the presence of stoechiometric amounts of titanium(IV) chloride [1].

General Procedure for the Reaction of α-Halomethyl Ketimines **3** and **5** with Potassium Thiocyanate.

A mixture of α-halomethyl ketimine **3** or **5** (0.005 mole) in acetonitrile (10 ml) (methanol was used in some experiments) was treated with potassium thiocyanate (0.0075 mole). The heterogeneous mixture was stirred at 60-70° during 1-2.5 hours (see Table I) after which the reaction mixture was poured into water. Extraction with dichloromethane, drying (magnesium sulfate) and evaporation of the solvent gave 3,4-disubstituted-2-imino-4-thiazolines **6** as dark viscous oils. The ^1H nmr analysis indicated a purity of >95%. Similar compounds, described in the literature, also were described as dark viscous oils [13,14]. All attempts to purify these materials resulted in partial decomposition (column chromatography, vacuum distillation).

4-*t*-Butyl-3-isopropyl-2-imino-4-thiazoline **6a** (R = *i*-Pr, R^1 = *t*-Bu).

This compound had ir (sodium chloride): ν 3320 (NH), 1583-1560 (C=C, C=N) cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.32 (s, 9H, *t*-Bu), 1.65 (d, 6H, Me_2, J = 7 Hz), 4.53 (septet, 1H, NCH, J = 7 Hz), 5.45 (s, 1H, S-CH=), 5.9 (1H, broad, NH); ^{13}C nmr (deuteriochloroform): δ 17.7 (Me_2), 29.7 (Me_3), 33.5 (*C*Me_3), 49.5 (NCH), 91.6 (S-CH=), 147.2 (N-*C*=C), 165.6 (C=N).

Anal. Calcd. for $C_{10}H_{18}N_2S$: N, 14.12. Found: N, 14.38.

4-*t*-Butyl-3-cyclohexyl-2-imino-4-thiazoline **6b** (R = cyclohex, R^1 = *t*-Bu).

This compound had ir (sodium chloride): ν 3330 (NH), 1586-1560 (C=C, C=N) cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.32 (s, 9H, *t*-Bu), 1.0-2.0 (m, 10H, $(CH_2)_5$), 3.0 (m, 1H, NCH), 5.2 (broad, 1H, NH), 5.42 (s, 1H, C-C*H*=); ms: m/z 238 (0.01), 228 (11), 227 (11), 177 (8), 176 (42), 175 (6), 156 (9), 141 (14), 135 (6), 134 (23), 112 (15), 105 (8), 104 (12), 91 (9), 79 (6), 77 (10), 72 (7), 57 (6), 56 (10), 55 (7), 45 (6), 44 (12), 43 (11), 41 (21), 40 (100), 39 (7).

3-Isopropyl-4-phenyl-2-imino-4-thiazoline **6c** (R = *i*-Pr, R^1 = Ph).

This compound had ir (sodium chloride): ν 3330 (NH), 1660-1550 (C=C, C=N) cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.44 (d, 6H, Me_2, J = 7 Hz), 4.13 (septet, 1H, NC*H*, J = 7 Hz), 5.5 (s, 1H, S-CH=), 6.5 (broad, 1H, NH), 7.35 (m, 5H, Ph); ^{13}C nmr (deuteriochloroform): δ 49.7 (N*C*H), 96.0 (S-*C*H=), 140.9 and 132.9 (N*C*=C and C_{quat}), 128.8 and 128.5 (*C*H= arom), 130.6 (*C*H= arom), 164.6 (*C*=N); ms: m/z 218 (23), 217 (19), 176 (80), 156 (19), 141 (42), 134 (54), 105 (21), 104 (22), 77 (20), 44 (13), 41 (42), 40 (100), 39 (15).

Anal. Calcd. for $C_{12}H_{14}N_2S$: N, 12.83. Found: N, 13.06.

2-Imino-3-isopropyl-4-(4-methylphenyl)-4-thiazoline **6d** (R = *i*-Pr, R^1 = *p*-MeC_6H_4).

This compound had ir (sodium chloride): ν 2970 (NH), 1595-1570 (C=C, C=N); ^1H nmr (deuteriochloroform): δ 1.46 (d, 6H, Me_2, J = 6.93 Hz), 2.40 (s, 3H, Me), 4.15 (septet, 1H, NCH, J = 6.93 Hz), 5.55 (s, 1H, S-CH=), 7.22 (s, 4H, C_6H_4 arom), NH invisible; ^{13}C nmr (deuteriochloroform): δ 19.1 (CH*Me*$_2$), 21.3 (Me), 49.9 (NCH), 96.0 (S-CH), 128.9 and 129.3

(each CH= arom), 129.4, 130.0 and 139.1 (each C_q=), 165.4 (C=N); ms: m/z 232 (21), 231 (20), 191 (12), 190 (100), 148 (41), 147 (22), 118 (18), 91 (16), 43 (14), 42 (13), 41 (25).

Anal. Calcd. for $C_{13}H_{16}N_2S$: N, 12.06. Found: N, 11.91.

4-*t*-Butyl-2-imino-3-isopropyl-4-methoxythiazolidine **10a** (R^1 = *t*-Bu; R = *i*-Pr).

When the synthesis of 2-imino-4-thiazoline **6a** (R = *i*-Pr, R^1 = *t*-Bu) was performed in methanol as solvent (see detailed procedure above), the reaction mixture contained variable amounts of the labile 4-*t*-butyl-2-imino-3-isopropyl-4-methoxythiazolidine **10a** (R^1 = *t*-Bu, R = *i*-Pr) (see text); ^{1}H nmr (carbon tetrachloride): δ 0.95 (s, 9H, *t*-Bu), 1.02 (d, 6H, Me_2, J = 6 Hz), 2.76 (septet, 1H, NCH, J = 6 Hz), 3.06 and 3.56 (each d, each 1H, CH_2, AB, J = 12 Hz), 3.84 (s, 3H, OMe), NH invisible. Attempts to isolate this methoxylated 2-iminothiazolidine **10a** by preparative gc resulted in conversion into the corresponding 2-imino-4-thiazoline **6a**.

General Procedure for the Reaction of α-Halomethyl Ketimines **3a** and **5** with Thiourea, Thioacetamide or Ammonium Thiocyanate.

The reactions of α-bromomethyl ketimine **3a** (R^1 = *t*-Bu, R = *i*-Pr) and α-chloromethyl ketimines **5** (R^1 = C_6H_5 or *p*-Me-C_6H_4, R = *i*-Pr) with thiourea, thioacetamide or ammonium thiocyanate were executed in a manner analogous to the procedure described above. Thus, the reaction of α-haloketimines **3a** and **5** with 1.5 molar equivalents of the above ambident nucleophiles in acetonitrile or methanol (10% solution w/v) was executed for a time described in the text. Aqueous workup and extraction with dichloromethane yielded, after drying (magnesium sulfate), the crude heterocycles (purity > 95%).

2-Amino-4-*t*-butylthiazole **11a**.

This compound had mp 100° (lit mp 99-101° [3,4]); ir (sodium chloride): ν 3120 and 3400 (NH), 1600-1635 and 1520 (C=C and C=N) cm^{-1}; ^{1}H nmr (carbon tetrachloride): δ 1.21 (s, 9H, *t*-Bu), 5.91 (s, 1H, S-CH), 6.0 (broad, 2H, NH_2); ^{13}C nmr (deuteriochloroform): δ 29.7 (Me_3), 34.5 (CMe_3), 99.0 (S-*C*H=), 162.1 and 168.0 (C=*C*-N and *C*=N); ms: m/z 156 (34), 141 (100), 114 (9), 113 (8), 99 (11), 97 (9), 65 (12), 45 (10), 41 (10), 40 (52), 39 (10).

2-Amino-4-phenylthiazole **11b**.

This compound was recrystallized from ethanol, mp 148.5-149.4° (lit mp 151° [15]); ir (potassium bromide): ν 3450 (NH), 1600 and 1520 (C=C and C=N) cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 5.30 (s, 2H, NH_2), 6.70 (s, 1H, S-CH), 7.25-7.40 (m, 3H, CH= arom), 7.76 (d, 2H, CH= arom, *meta*, J = 7.26 Hz); ^{13}C nmr (deuteriochloroform): δ 102.8 (S-CH), 126.0, 127.7 and 128.6 (each CH= arom), 134.7 (Cq=), 151.4 and 167.5 (-N=C and N-C=); ms: m/z 176 (100), 175 (6), 134 (55), 133 (3), 108 (3), 104 (10), 90 (12), 89 (13), 88 (6), 77 (6), 69 (4), 63 (5), 51 (6), 45 (4).

2-Amino-4-(4-methylphenyl)thiazole **11c**.

This compound was recrystallized from ethanol, mp 133.5-134.8° (lit mp 130-131° [15]); ir (potassium bromide): ν 3450 (NH), 1625 and 1585 (C=C and C=N) cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 2.36 (s, 3H, Me), 5.16 (br s, 2H, NH_2), 6.65 (s, 1H, S-CH), 7.18 (d, 2H, CH= arom, *ortho*, J = 7.92 Hz), 7.66 (d, 2H, CH= arom, *meta*, J = 7.92 Hz); ^{13}C nmr (deuteriochloroform): δ 21.2 (Me), 102.0 (S-CH=), 125.9 and 129.3 (each CH=), 132.0 and 137.5 (each C_q=), 151.4 (N-C=), 167.3 (C=N); ms: m/z 190 (100), 189 (5), 149 (5), 148 (35), 147 (31), 118 (8), 115 (7), 104 (6), 103 (6), 94 (7), 91 (12), 77 (6), 45 (6).

2-Methyl-4-*t*-butylthiazole **12a**.

This compound had ir (sodium chloride): ν 1515 (arom); ^{1}H nmr (carbon tetrachloride): δ 1.31 (s, 9H, *t*-Bu), 3.66 (s, 3H, Me), 6.66 (s, 1H, S-CH=); ^{13}C nmr (deuteriochloroform): δ 19.1 (Me), 30.0 (Me_3), 34.6 (CMe_3), 109.4 (S-*C*H=), 164.6 and 166.3 (*C*=N and N-*C*=); ms: m/z 155 (28), 140 (100), 123 (6), 99 (13), 97 (7), 91 (5), 65 (20), 59 (14), 58 (8), 57 (9), 55 (6), 53 (8), 45 (28), 42 (13), 41 (25), 40 (16), 39 (27).

Anal. Calcd. for $C_8H_{13}NS$: N, 9.02. Found: N, 8.87.

2-Methyl-4-phenylthiazole **12b**.

This compound was recrystallized from ethanol, mp 66.7-67.8°; ir (potassium bromide): ν 1498 (arom) cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 2.76 (s, 3H, Me), 7.29 (s, 1H, S-CH=), 7.25-7.43 (m, 3H, CH= arom, *ortho* + *para*), 7.85-7.89 (m, 2H, CH= arom, *meta*); ^{13}C nmr (deuteriochloroform): δ 19.3 (Me), 112.2 (S-CH=), 126.4, 128.0 and 128.7 (each CH= arom), 134.6 (C_q=), 155.2 and 165.8 (C=N and N-C=); ms: m/z 175 (71), 136 (5), 134 (100), 90 (13), 89 (16), 88 (5), 69 (5), 67 (11), 63 (6), 51 (6).

2-Methyl-4-(4-methylphenyl)thiazole **12c**.

This compound was recrystallized from ethanol, mp 53.1-55.0°; ir (potassium bromide): ν 1500 (arom) cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 2.37 (s, 3H, Me), 2.76 (s, 3H, S-C*Me*), 7.22 (d, 2H, CH= arom, *ortho*, J = 7.92 Hz), 7.26 (s, 1H, S-CH), 7.77 (d, 2H, CH= arom, *meta*, J = 7.92 Hz); ^{13}C nmr (deuteriochloroform): δ 19.3 (S-C*Me*), 21.2 (Me), 11.4 (S-CH), 126.2 and 129.4 (each CH= arom), 131.9 and 137.8 (each C_q=), 155.3 and 165.7 (*C*=N and N-*C*=); ms: m/z 189 (100), 149 (13), 148 (81), 147 (48), 119 (10), 103 (7), 94 (9), 91 (14), 77 (6), 45 (5).

General Procedure for the Reaction of α-Halomethyl Ketimines **3a** and **5** with Potassium Cyanate.

The reaction was run in the same way as described for the reactions with potassium thiocyanate. Aqueous workup afforded 1-isopropyl-4-imidazolin-2-ones **17**.

5-*t*-Butyl-1-isopropyl-4-imidazolin-2-one **17a**.

This compound was recrystallized from diethyl ether (-20°), mp 211°; ir (sodium chloride): ν 3120 (NH), 1660-1680 (C=O, C=C) cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 1.24 (s, 9H, *t*-Bu), 1.55 (d, 6H, Me_2, J = 7 Hz), 4.32 (septet, 1H, NC*H*, J = 7 Hz), 5.9 (broad s, 1H, N*H*), 5.95 (s, 1H, C*H*=); ^{13}C nmr (deuteriochloroform): δ 19.5 (Me_2), 29.6 (Me_3), 30.6 (CMe_3), 47.1 (NCH), 102.8 (O-*C*H=), 131.5 (N-*C*=C), 155.8 (*C*=N); ms: m/z 182 (18), 140 (15), 125 (9), 44 (9), 43 (18), 42 (12), 41 (29), 40 (100).

Anal. Calcd. for $C_{10}H_{18}N_2O$: N, 15.37. Found: N, 15.19.

5-Phenyl-1-isopropyl-4-imidazolin-2-one **17b**.

This compound was recrystallized from ethanol, mp 251.3-252.2°; ir (potassium bromide): ν 3110 (NH), 1650-1670 (C=O and C=C) cm^{-1}; ^{1}H nmr (deuteriochloroform): δ 1.48 (d, 6H, Me_2, J = 6.93 Hz), 4.16 (septet, 1H, NC*H*Me_2, J = 6.93 Hz), 6.26 (d, 1H, NH-C*H*=, J = 2.31 Hz), 7.26-7.44 (m, 5H, CH= arom), 10.64 (broad s, 1H, NH); ^{13}C nmr (deuteriochloroform): δ 20.5 (Me_2), 46.3 (NCHMe_2), 106.2 (NH-*C*H=), 128.1, 128.6 and 129.2 (each CH= arom), 125.6 and 130.5 (each C_q=), 155.1

(C=O); ms: m/z 202 (42), 160 (100), 159 (4), 132 (5), 117 (4), 104 (48), 89 (4), 77 (12), 43 (5), 42 (5), 41 (9).

Anal. Calcd. for $C_{12}H_{14}N_2O$: N, 13.85. Found: N, 13.74.

5-(4-Methylphenyl)-1-isopropyl-4-imidazolin-2-one **17c**.

This compound was recrystallized from ethanol, mp 197.8-199.3°; ir (potassium bromide): ν 3120 (NH), 1615-1650 (C=O and C=C) cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.46 (d, 6H, Me_2, J = 6.93 Hz), 2.39 (s, 3H, Me), 4.14 (septet, 1H, NC*H*Me_2, J = 6.93 Hz), 6.22 (t, 1H, NH-C*H*=, J = 2.31 Hz), 7.21 (broad s, 4H, CH= arom), 11.59 (broad s, 1H, NH); ^{13}C nmr (deuteriochloroform): δ 20.5 (Me_2), 21.2 (Me), 46.2 (N*C*HMe_2), 106.1 (NH-*C*H=), 125.4, 127.6 and 138.1 (each C_q=), 129.2 (CH= arom), 155.2 (C=O); ms: m/z 216 (43), 174 (100), 173 (6), 146 (4), 130 (5), 119 (5), 118 (33), 91 (6), 41 (6).

Anal. Calcd. for $C_{13}H_{16}N_2O$: N, 12.95. Found: N, 13.09.

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