A Convenient Preparation of 4-Methyl- and 4-Phenylseleno-1,1,1-trihalo-3-alken-2-ones and their Usefulness in the Synthesis of 3-Trihalomethyl-isoselenazoles

Marcos A. P. Martins,* Giovani P. Bastos, Adilson P. Sinhorin, Nilo E. K. Zimmermann, Helio G. Bonacorso, Nilo Zanatta

Núcleo de Química de Heterociclos (NUQUIMHE), Departamento de Química, Universidade Federal de Santa Maria, 97.105-900 Santa Maria, RS, Brazil
Fax +55(55)2208031; E-mail: mmartins@base.ufsm.br
Received 28 February 2002; revised 27 May 2002

Abstract: A convenient synthesis of fourteen 4-methyl- and 4-phenylseleno-1,1,1-trihalo-3-alken-2-ones [$CX_3C(O)CH=CR^1SeR$, where X = F, Cl; R = Me, Ph; and R^1 = H, alkyl, aryl] from the reaction of the corresponding 4-methoxy-1,1,1-trihalo-3-alken-2-ones with methyl- or phenylselenols in the presence of boron trifluoride etherate is reported. The reaction of 4-methylseleno-1,1,1-trihalo-3-alken-2-ones with bromine and ammonia lead to 3-trihalomethylisoselenazoles in good yields. The usefulness of the trichloromethyl group as a carboxyl group precursor was demonstrated by the conversion of 5-ethyl-3-trichloromethylisoselenazole to 5-ethyl-3-carboxyisoselenazole acid.

Key words: isoselenazoles, selenium, enones, halogens, heterocycles

Organoselenium compounds are useful intermediates in organic synthesis.[1–4] The reactivity of the organoselenium compounds is mainly associated with the ability of selenium to stabilize adjacent positive and negative charges, as well as with the ease of selenides to undergo oxidation to selenoxides with subsequent facile selenoxide *syn*-elimination. The development of general and efficient methods for large-scale preparation of important substrates such as alkyl- and arylselenovinyl ketones (or aldehydes) has been the subject of increasing interest. These intermediates have been used as potential precursors for a variety of substituted five-membered heterocyclic compounds, e.g., isoselenazoles and 1,2-benzoselenazoles.[5] The synthesis of β-methylselenovinyl ketones from the substitution of β-halovinyl ketones with methylselenol, has been reported in the literature.[5] Homoallyl alcohol has been transformed to the corresponding methyl- or phenylselenyl compounds from the reaction of the corresponding selenol in the presence of boron trifluoride etherate.[6] β-Phenylseleno α,β-unsaturated cycloalkanones have also been obtained from the reaction of β-halocycloalkenones with nucleophilic selenium reagents.[7–9] As a part of our research program, we developed a general synthesis of 4-methoxy-1,1,1-trihalo-3-alken-2-ones[10,11] and their usefulness in heterocyclic preparations has been shown.[10,12–14] The transformation of the trichloromethyl group under mild conditions[14] into carboxylic groups prompted us to devote special attention to these substrates. The aim of this work is to report the synthesis of 4-methyl- and 4-phenylseleno-1,1,1-trihalo-3-alken-2-ones **2a**–**n** from the reaction of the corresponding 4-methoxy-1,1,1-trihalo-3-alken-2-ones **1a**–**n** with selenium nucleophiles in the presence of boron trifluoride etherate (Scheme 1).

The advantage of our methodology if compared with the literature methods is the facile access to several substrate structures and the preparation of trihalomethyl containing compounds. The reaction of 4-methylseleno-1,1,1-trihalo-3-alken-2-ones **2g,i,k**–**n** with bromine and ammonia lead to 3-trihalomethylisoselenazoles **3g,i,k**–**n** as presented in Scheme 1.

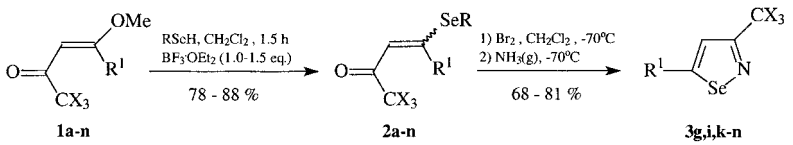
The 4-methoxy-1,1,1-trihalo-3-alken-2-ones **1a**–**n** were synthesized from the reaction of the proper enol ether or acetal with trifluoroacetic anhydride or trichloroacetyl chloride.[10,11]

The reactions of compounds **1** with methyl- and phenylselenol were carried out at room temperature using equimolar amount of the reagents and boron trifluoride etherate in dichloromethane. However, in the reactions of compounds **1c**,**i**–**m** 1.5 equivalents of boron trifluoride etherate were necessary. The reaction of compounds **1b**,**c**,**f**–**h**,**j**–**n** with methyl- and phenylselenols led regiospecifically to the products **2** with *Z*-configuration and the reaction of compounds **1a**,**d**,**e**,**i** with selenols furnished a mixture of compounds **2***Z* and **2***E* in a molar ratio of approximately 3: 1, respectively (see Table 1). In order to show the usefulness of compounds **2** to obtain isoselenazoles **3**, we performed cyclo-condensation of **2g,i,k**–**n** according with methodology developed by Weber et. al.,[5] where compounds **2** react with bromine in dichloromethane at –70 °C and, in a second step, at the same temperature, an excess of ammonia is bubbled in the mixture (Scheme 1).

Finally, considering the importance of isoselenazolecarboxylic acids[15] and according with methodology developed in our laboratory[14] to obtain carboxyalkylisoxazoles and carboxyalkylpyrazoles from trichloromethylazoles, we show the synthesis of compound **4k** from the compound **3k** in good yield (Scheme 2). The reaction was carried out in 96% sulfuric acid (acid–selenoisoxazole; 3:1) in water at room temperature for 24 hours.

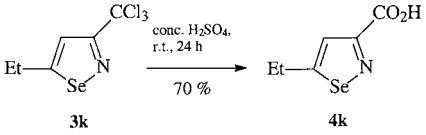
Synthesis 2002, No. 15, Print: 29 10 2002.
Art Id.1437-210X,E;2002,0,15,2220,2224,ftx,en;M00402SS.pdf.

ISSN 0039-7881



	2	2, 3, 4	2, 3
	R	R^1	X
a	Ph	H	F
b	Ph	4-F-C_6H_4	F
c	Ph	CH_3	Cl
d	CH_3	H	F
e	CH_3	CH_3	F
f	CH_3	Ph	F
g	CH_3	4-F-C_6H_4	F
h	CH_3	4-Cl-C_6H_4	F
i	CH_3	H	Cl
j	CH_3	CH_3	Cl
k	CH_3	CH_2CH_3	Cl
l	CH_3	$CH(CH_3)_2$	Cl
m	CH_3	$CH_2CH(CH_3)_2$	Cl
n	CH_3	Ph	Cl

Scheme 1



Scheme 2

Unless otherwise indicated all common reagents and solvents were used as obtained from commercial suppliers without further purification. All mps were determined on a Reichert Thermovar apparatus. Selected physical and spectral data are presented in Tables 1 and 2. ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX-200 (^1H at 200.13 MHz and ^{13}C at 50.32 MHz), 298 K, digital resolution ± 0.01 ppm, 0.5 M in carbon tetrachloride–TMS (with benzene-d_6 for lock in a capillary tube). IR spectra were obtained on a Perkin–Elmer 599-B. Satisfactory elemental analyses (C ± 0.30, H ± 0.20) were obtained for all compounds.

4-Methyl- and 4-Phenylseleno-1,1,1-trihalo-3-alken-2-ones 2a–n; General Procedure

To a stirred solution of 4-methoxy-1,1,1-trihalomethyl-4-methoxy-3-alken-2-ones **1a–n** (10 mmol), methyl- or phenylselenol (10 mmol) in CH_2Cl_2 (10 mL), at 20 °C and under nitrogen atmosphere, $BF_3{\cdot}OEt_2$ (10 mmol, 15 mmol for compounds **1c**,**i**,**j**–**m**) was added dropwise. The mixture was stirred for 1.5 h at r.t., then the mixture was washed with aq Na_2CO_3 (5%; 2 × 10 mL) and H_2O (2 × 10 mL). The organic phase was dried (Na_2SO_4) and the solvent was removed. The products **2a**,**b**,**d** were recrystallized from hexane–EtOAc and the products **2c**,**e**–**n** were purified by column chromatography (silica gel 70–230 mesh; hexane–$CHCl_3$, 1:1). Yields, selected physical and spectral data are presented in Table 1.

Table 1 Selected Physical and Spectral Data of **2**

Product	MF/MW	Yield[a] (%)	Mp (°C)	IR (film) (cm^{-1})	^1H NMR δ, *J* (Hz)	^{13}C NMR δ, *J* (Hz)
2a *Z*	$C_{10}H_7F_3OSe$ (279.12)	84	28–32	1770, 1680, 1661	7.14 (d,1 H, *J* = 8.6, H-3), 8.59 (d, 1 H, *J* = 8.6, H-4), 7.39 (m, 5 H, SePh)	116.2 (q, $^1J_{CF}$ = 289.3, C-1), 179.3 (q, $^2J_{CF}$ = 35.8, C-2), 118.8 (C-3),163.6 (C-4), 127.6, 129.6, 129.9, 135.2 (SePh)
2a *E*	$C_{10}H_7F_3OSe$ (279.12)				6.90 (d, 1 H, *J* = 15.0, H-3), 8.76 (d, 1 H, *J* = 15.0, H-4), 7.61 (m, SePh)	115.9 (q, $^1J_{CF}$ = 279.1, C-1), 176.0 (q, $^2J_{CF}$ = 35.1, C-2), 113.2 (C-3), 156.2 (C-4), 124.6, 129.6, 129.9, 135.2 (SePh)

Table 1 Selected Physical and Spectral Data of **2** (continued)

Product	MF/MW	Yield[a] (%)	Mp (°C)	IR (film) (cm^{-1})	^1H NMR δ, *J* (Hz)	^{13}C NMR δ, *J* (Hz)
2b	$C_{16}H_{10}F_4OSe$ (373.21)	82	40 – 43	1761, 1617	7.11 (s, 1 H, H-3), (m, 4 H, Ph), 7.24 (m, 5 H, SePh)	127.1 ($^1J_{CF}$ = 282.6, C-1), 176.6 ($^2J_{CF}$ = 35.2, C-2), 113.6 (C-3), 173.2 (C-4), 126.7, 127.9, 129.1, 135.0 (SePh)
2c	$C_{11}H_{11}Cl_3OSe$ (344.52)	83	48– 50	1755, 1663	7.38 (s, 1 H, H-3), 2.12 (s, 3 H, H-5), 7.20–7.72 (m, 5 H, SePh)	92.9 (C-1), 173.3 (C-2), 113.8 (C-3), 179.5 (C-4), 22.7 (C-5), 127.6, 128.9, 129.3, 137.8 (SePh)
2d *Z*	$C_5H_5F_3OSe$ (217.05)	79	Oil	1766, 1671, 1521	7.06 (d, 1 H, *J* = 9.3, H-3), 8.51 (d, 1 H, *J* = 9.3, H-4), 2,41 (s, 3 H, $SeCH_3$)	116.1 (q, $^1J_{CF}$ = 286.6, C-1), 179.1 (q, $^2J_{CF}$ = 35.1, C2), 114.7 (C-3), 162.3 (C-4), 10.8 ($SeCH_3$)
2d *E*	$C_5H_5F_3OSe$ (217.05)				6.54 (d, 1 H, *J* = 15.3, H-3), 8.69 (d, 1 H, *J* = 15.3, H-4), 2.41 (s, 3 H $SeCH_3$)	115.6 (q, $^1J_{CF}$ = 280.0, C-1), 177.2 (q, $^2J_{CF}$ = 34.0, C-2), 112.8 (C-3), 160.3 (C-4), 6.41 (C-5) ($SeCH_3$)
2e *Z*	$C_6H_7F_3OSe$ (231.08)	80	Oil	1688, 1577	6.65 (s, 1 H, H-3), 2.45 (s, 3 H, H-5), 2.23 (s, 3 H, $SeCH_3$)	115.3 (q, $^1J_{CF}$ = 287.4, C-1), 177.0 (q, $^2J_{CF}$ = 35.5, C-2), 112.4 (C-3), 160.5 (C-4), 26.2 (C-5), 5.97 ($SeCH_3$)
2e *E*	$C_6H_7F_3OSe$ (231.08)				6.88 (s, 1 H, H-3), 2.57 (s, 3 H, H-5), 2.27 (s, 3 H, $SeCH_3$)	118.9 (q, $^1J_{CF}$ = 278.2, C-1), 179.1 (q, $^2J_{CF}$ = 34.7, C-2), 115.7 (C-3), 175.3 (C-4), 29.4 (C-5), 6.99 ($SeCH_3$)
2f	$C_{11}H_9F_3OSe$ (293.14)	88	Oil	1698, 1597, 1471	7.46 (s, 1 H, H-3), 7.52 (m, 5 H, Ph), 1.97 (s, 3 H, $SeCH_3$)	129.5 (q, $^1J_{CF}$ = 288.4, C-1), 177.8 (q, $^2J_{CF}$ = 36.1, C-2), 117.3 (C-3), 186.4 (C-4), 128.6, 127.7, 139.8 (Ph), 9.02 ($SeCH_3$)
2g	$C_{11}H_8F_4OSe$ (311.14)	87	Oil	1601, 1533, 1501	6.92 (s,1 H, H-3), 7.17 (m, 4 H, Ph), 1.78 (s, 3 H, $SeCH_3$)	116.8 (q, $^1J_{CF}$ = 289.1, C-1), 177.1 (q, $^2J_{CF}$ = 35.4, C-2), 117.5(C-3), 185.5 (C-4), 8.82 ($SeCH_3$), 127.5, 128.5, 130.5, 135.6 (Ph)
2h	$C_{11}H_8F_3ClOSe$ (327.59)	82	Oil	1650, 1594, 1481	6.92 (s, 1 H, H-3), 7.23–7.58 (m, 4 H, Ph), 1.79 (s, 3 H, $SeCH_3$)	127.1 (q, $^1J_{CF}$ = 289.4, C-1), 178.5 (q, $^2J_{CF}$ = 34.9, C-2), 117.3 (C-3), 185.1 (C-4), 127.5, 128.4, 129.7, 137.9 (Ph)
2i *Z*	$C_5H_5Cl_3OSe$ (266.41)	84	Oil	1699, 1677, 1518	7.26 (d, 1 H, *J* = 9.2, H-3), 8.31 (d, 1 H, *J* = 9.2, H-4), 2.29 (s, 3 H, $SeCH_3$)	96.4 (C-1), 179.9 (C-2), 115.7 (C-3), 160.9 (C-4), 10.5 ($SeCH_3$)
2i *E*	$C_5H_5Cl_3OSe$ (266.41)				6.76 (d, 1 H, *J* = 5.0, H-3), 8.54 (d, 1 H, *J* = 15.0, H-5), 2.27 (s, 3 H, $SeCH_3$)	97.5 (C-1), 175.7 (C-2), 116.9 (C-3), 158.3 (C-4), 6.93 ($SeCH_3$)
2j	$C_6H_7Cl_3OSe$ (280.44)	85	Oil	1697, 1612	6.76 (s, 1 H, H-3), 1.80 (s, 3 H, H-5), 1.71 (s, 3 H, $SeCH_3$)	93.4 (C-1), 159.4 (C-2), 114.5 (C-3), 179.6 (C-4), 26.4 (C-5), 6.04 ($SeCH_3$)
2k	$C_7H_9Cl_3OSe$ (294.46)	81	Oil	1690, 1622	7.18 (s, 1 H, H3), 2.72 (q, 2 H, *J* = 7, H-5), 2.25 (s, 3 H, $SeCH_3$), 1.21 (t, 3 H, *J* = 7, H-6)	91.4 (C-1), 175.2 (C-2), 112.5 (C-3), 191.5 (C-4), 31.6 (C-5), 14.2 (C-6), 5.43 ($SeCH_3$)
2l	$C_8H_{11}Cl_3OSe$ (308.49)	82	Oil	1632, 1512, 1476	7.10 (s, 1 H, H-3), 3.00 (sep, 1 H, *J* = 7, H-5), 1.26 (d, 6 H, *J* = 7, H-6), 2.15 (s, 3 H, $SeCH_3$)	90.3 (C-1), 181.0 (C-2), 110.9 (C-3), 178.4 (C-4), 34.9 (C-5), 23.6 (C-6), 5.76 ($SeCH_3$)
2m	$C_9H_{13}Cl_3OSe$ (322.52)	79	Oil	1682, 1572, 1426	7.12 (s, 1 H, H-3), 2.64 (d, 2 H, *J* = 7, H-5), 2.01 (m, 1 H, H-6), 1.13 (d, 6 H, *J* = 7, H-7), 2.33 (s, 3 H, $SeCH_3$)	93.3 (C-1), 188.7 (C-2), 115.1 (C-3), 173.4 (C-4), 29.5 (C-5), 46.1 (C-6), 23.0 (C-7), 5.83 ($SeCH_3$)
2n	$C_{11}H_9Cl_3OSe$ (342.51)	81	71– 75	1702, 1623	7.35 (s, 1 H, H-3), 7.47 (m, 5 H, Ph), 1.90 (s, 3 H, $SeCH_3$)	89.3 (C-1), 160.5 (C-2), 116.1 (C-3), 179.9 (C-4), 128.5, 127.7, 128.2, 139.0 (Ph), 8.32 ($SeCH_3$)

[a] Yields are of isolated compounds and refers to a mixture of *Z* and *E* isomers.

Table 2 Selected Physical and Spectral Data of **3, 4**

Product	MF/MW	Mp (°C)	Yield[a] (%)	CG–MS *m/z* (%)	^{1}H NMR δ, *J* (Hz)	^{13}C NMR δ, *J* (Hz)
3g	$C_{10}H_5F_4NSe$ 294.11	48– 51	66	295 (M^+, 100), 276 (10), 226 (5)	7.63 (s, 1 H, H-4), 7.07 (d, 4 H, Ph), 7.39 (m, 5 H, SePh)	161.3 (q, ^2J = 35.7, C3),122.7 (C4), 176.2 (C5), 116.3, 116.9, 128.7, 132.5 (Ph), 120.0 (q, ^1J = 275.2, CF_3)
3i	$C_4H_2Cl_3NSe$ 249.38	40– 43	72	249 (M^+, 40), 214 (100)	7.33 (d, 1 H, *J* = 6.8, H-5), 7.90 (d, 1 H, *J* = 6.8, H4)	153.1 (C3), 115.4 (C4), 161.5 (C5), 96.9 (CCl_3)
3k	$C_6H_6Cl_3NSe$ 277.44	Oil	81	277 (M^+, 33), 242 (100), 158 (40)	7.61 (s, 1 H, H4), 3.00 (q, 2 H, H6), 1.43 (t, 3 H, H7)	167.1 (C3), 121.1 (C4), 183.1 (C5), 25.0 (C6), 15.9 (C7), 91.4 (CCl_3)
3l	$C_7H_8Cl_3NSe$ 291.46	Oil	68	291 (M^+,10), 256 (100)	7.52 (s, 1 H, H4), 2.19 (sep, 1 H, H6), 1.41 (d, 6 H, H7)	168.3 (C3), 120.5 (C4), 187.2 (C5), 35.1 (C6), 25.8 (C7), 90.3 (CCl_3)
3m	$C_8H_{10}Cl_3NSe$ 305.49	Oil	74	305 (M^+,15), 270 (100), 227 (25), 119 (15)	7.34 (s, 1 H, H4), 2.70 (d, 2 H, H6), 2.16 (m, 1 H, H7), 1.03 (d, 6 H, H8)	168.2 (C3), 122.3 (C4), 183.7 (C5), 27.5 (C6), 42.8 (C7), 23.1 (C8), 94.0 (CCl_3)
3n	$C_{10}H_6Cl_3NSe$ 325.48	82– 75	69	325 (M^+, 20), 290 (100), 207 (5), 140 (30)	8.00 (s, 1 H, H4), 7.37 (m, 5 H, Ph)	153.1 (C3), 120.4 (C4), 176.5 (C5), 127.4, 127.9, 130.5, 139.4 (Ph), 90.0 (CCl_3)
4k	$C_6H_7NO_2Se$ 204.08	136–138	70	205 (M^+, 25), 133 (22), 80 (100)	7.66 (s, 1 H, H4), 3.10 (q, 2 H, H6), 1.25 (t, 3 H, H7)	173,1 (C3), 119,5 (C4), 160.2 (C5), 32.8 (C6), 19.0 (C7), 173.0 (C=O)

[a] Yields are of isolated compounds.

3-Trihalomethylisoselenazoles 3g,i,k–n; General Procedure

A three-necked flask containing a solution of 4-methylseleno-1,1,1-trihalo-3-alken-2-ones **2g**,**i**,**k**–**n** (5 mmol) in CH_2Cl_2 (20 mL) was cooled to –70 °C. Bromine (5 mmol) in CH_2Cl_2 (10 mL) was added dropwise to this stirred solution. After a few minutes, an excess of ammonia was bubbled in the mixture, which was then allowed to reach r.t.. H_2O (50 ml) was added, and the organic phase separated and dried ($MgSO_4$). Products **3g**,**i**,**k**–**n** were obtained after distilling off the solvent and separation by chromatographic column (silica gel; cyclohexane–EtOAc). Yields, selected physical and spectral data are presented in Table 2.

5-Ethyl-3-carboxyisoselenazole Acid (4k)

To a stirred solution of 5-ethyl-3-trichloromethylisoselenazole (**3k**) (5 mmol), a solution of H_2SO_4 (96%; 1.47 g, 15 mmol) and H_2O (0.8 mL) (1:1 v/v) at r.t. was added. The mixture was refluxed for 24 h and then extracted with $CHCl_3$. The organic phase was then washed with H_2O (3 × 10 mL) and aq Na_2CO_3 (5%; 1 × 10 mL). The organic phase was dried (Na_2SO_4) and the solvent was removed on a rotary evaporator. After evaporation of the solvent, the product **4k** was recrystallized from cyclohexane. Yields, selected physical and spectral data are presented in Table 2.

Acknowledgments

The authors thank the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq/PADCT III, contract No. 62.0228/97-0; and CNPq Contract No. 46.0804/00-6), Fundação de Amparo à Pesquisa do Estado do Rio Grande do Sul (FAPERGS) for financial support and fellowships.

References

(1) Patai, S.; Rappoport, Z. *The Chemistry of Organic Selenium and Tellurium Compounds*; Wiley: New York, **1986**.
(2) Paulmier, C. *Selenium Reagents and Intermediates in Organic Synthesis*; Pergamon: Oxford, **1986**.
(3) Liotta, D. *Organoselenium Chemistry*; Wiley: New York, **1987**.
(4) Krief, A.; Hevesi, L. *Organoselenium Chemistry*; Springer: Berlin, **1988**.
(5) Weber, R.; Renson, M. *J. Heterocycl. Chem.* **1973**, *10*, 267.
(6) Krief, A.; Hobe, M.; Badaoui, E.; Bousbaa, J.; Dumont, W.; Nazih, A. *Synlett* **1993**, 707.
(7) Shimizu, M.; Ando, R.; Kuwajima, I. *J. Org. Chem.* **1984**, *49*, 1230.
(8) Hamaguchi, M.; Nagai, T. *J. Org. Chem.* **1989**, *54*, 3957.
(9) Sakakibara, M.; Katsumita, K.; Watanabe, Y.; Toru, T.; Ueno, Y. *Synthesis* **1992**, 377.
(10) Colla, A.; Martins, M. A. P.; Clar, G.; Krimmer, S.; Fischer, P. *Synthesis* **1991**, *6*, 483.
(11) (a) Martins, M. A. P.; Bastos, G. P.; Bonacorso, H. G.; Zanatta, N.; Flores, A. F. C.; Siqueira, G. M. *Tetrahedron Lett.* **1999**, *40*, 4309. (b) Bonacorso, H. G.; Martins, M. A. P.; Bittencourt, S. R. T.; Lourega, R. V.; Zanatta, N.; Flores, A. F. C. *J. Fluorine Chem.* **1999**, *99*, 177. (c) Martins, M. A. P.; Siqueira, G. M.; Flores, A. F. C.; Clar, G.; Zanatta, N. *Química Nova* **1994**, *17*, 24.
(12) (a) Martins, M. A. P.; Zoch, A. N.; Bonacorso, H. G.; Zanatta, N.; Clar, G. *J. Heterocycl. Chem.* **1995**, *32*, 739. (b) Martins, M. A. P.; Flores, A. F. C.; Freitag, R.; Zanatta, N. *J. Heterocycl. Chem.* **1995**, *32*, 731. (c) Martins, M. A. P.; Flores, A. F. C.; Freitag, R.; Zanatta, N. *J. Heterocycl. Chem*. **1996**, *33*, 1223. (d) Martins, M. A. P.; Siqueira, G.

M.; Bastos, G. P.; Zanatta, N. *J. Heterocycl. Chem.* **1996**, *33*, 1619. (e) Braibante, M. E. F.; Martins, M. A. P.; Clar, G. *J. Heterocycl. Chem.* **1993**, *30*, 1159.

(13) (a) Zanatta, N.; Pacholski, I. L.; Blanco, I.; Martins, M. A. P. *J. Braz. Chem. Soc.* **1991**, *1*, 118. (b) Zanatta, N.; Madruga, C. C.; Clerici, E.; Martins, M. A. P. *J. Heterocycl. Chem.* **1995**, *32*, 735. (c) Zanatta, N.; Cortelini, M. F. M.; Carpes, M. J. S.; Bonacorso, H. G.; Martins, M. A. P. *J. Heterocycl. Chem.* **1997**, *34*, 509. (d) Bonacorso, H. G.; Bittencourt, S. T.; Wastowski, A. D.; Wentz, A. P.; Zanatta, N.; Martins, M. A. P. *Tetrahedron Lett.* **1996**, *37*, 9155. (e) Zanatta, N.; Fagundes, M. B.; Ellenshon, R.; Marques, M.; Bonacorso, H. G.; Martins, M. A. P. *J. Heterocycl. Chem.* **1998**, *35*, 451.

(14) (a) Martins, M. A. P.; Flores, A. F. C.; Bastos, G. P.; Sinhorin, A.; Bonacorso, H. G.; Zanatta, N. *Tetrahedron Lett.* **2000**, *41*, 293. (b) Martins, M. A. P.; Freitag, R. A.; Rosa, A.; Flores, A. F. C.; Zanatta, N.; Bonacorso, H. G. *J. Heterocycl. Chem.* **1995**, *32*, 731. (c) Martins, M. A. P.; Freitag, R. A.; Flores, A. F. C.; Zanatta, N. *Synthesis* **1995**, 1491.

(15) Lucchesini, F.; Bertini, V.; De Munno, A. *Heterocycles* **1985**, *23*, 127.