Pergamon

Tetrahedron Letters 43 (2002) 7005–7008

TETRAHEDRON LETTERS

Microwave assisted synthesis of 5-hydroxy-5-trichloromethyl-4,5-dihydroisoxazoles

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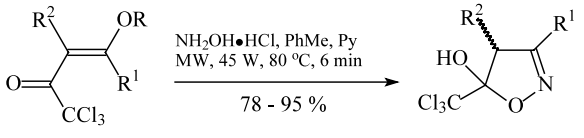
Received 27 May 2002; accepted 29 July 2002

Abstract—A series of 13 5-hydroxy-5-trichloromethyl-4,5-dihydroisoxazoles have been synthesized in 78–96% yield by environmentally benign microwave induced techniques involving the cyclocondensation of 4-alkoxy-1,1,1-trichloro-3-alken-2-ones [$CCl_3C(O)C(R^2)=C(R^1)OR$, where $R^2=H$, alkyl; $R^1=H$, alkyl, aryl and $R=H$, alkyl] with hydroxylamine using toluene as solvent. The advantages obtained by the use of microwave irradiation in relation to a classical method were demonstrated.

Isoxazoles and their derivatives have been recognized as highly useful in medicinal chemistry, in particular, many trihalomethylated azoles are known to exhibit important biological activities in medicinal and agricultural scientific fields.[1–3] The synthesis of isoxazoles through route [3+2] uses, in general, derived of β-diketones as block CCC, and the hydroxylamine as block NO.[4] In recent years, we have developed a general synthesis of a large number of 1,1,1-trihalo-4-methoxy-3-alken-2-ones,[5,6] important halogen-containing building blocks, and demonstrated their usefulness in heterocyclic preparations, e.g. isoxazoles,[5,7,8] pyrazoles,[9] pyrazolium chlorides,[10] pyrrolidinones,[11] pyrimidines,[12] pyridines,[13] thiazines[14] and diazepines.[15] Although most research groups have published papers almost exclusively with fluorinated derivatives[16] of 1,1,1-trihalo-4-methoxy-3-alken-2-ones, the possibility of the transformation of the trichloromethyl group under mild conditions[8,17,18] into carboxylic groups prompted us to devote special attention to these substrates. In 1986 Spiegler and Götz[19] reported the first work which showed the synthesis of 5-hydroxy-5-trichloromethyl-4,5-dihydroisoxazoles from the reaction of 4-ethoxy-1,1,1-trichloro-3-buten-2-one (obtained in situ from the trichloroacetylation of ethyl vinyl ether) with hydroxylamine hydrochloride, in water at room temperature, with a reaction time of 24 h. However, this reaction was an isolated result using only one substrate and did not demonstrate the real scope of the reaction. Since 1991 the scope of this reaction has been extended in our laboratory with the publication of a series of papers about the synthesis of 5-hydroxy-5-trichloromethyl-4,5-dihydroisoxazoles using a *classical method*, where the 4-alkoxy-1,1,1-trichloro-3-alken-2-ones reacted with a saturated aqueous solution of hydroxylamine hydrochloride, in



1a-m **2a-m**

	R	R^1	R^2		R	R^1	R^2
a	Et	H	H	**h**	Me	*iso*-Bu	H
b	Me	Me	H	**i**	Me	*tert*-Bu	H
c	Me	Et	H	**j**	Me	*n*-Hex	H
d	Me	*n*-Pr	H	**k**	Me	Ph	H
e	Me	*iso*-Pr	H	**l**	Me	*p*-O_2N-C_6H_4	H
f	Me	*cyclo*-Pr	H	**m**	H	-$(CH_2)_4$-	
g	Me	*n*-Bu	H				

Scheme 1.

Keywords: microwave irradiations; isoxazoles; enones; halogen compounds.

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0040-4039/02/$ - see front matter
PII: S0040-4039(02)01555-1

Table 1. Yields[a] and reaction conditions used for the microwave assisted synthesis of **2a–m**

Microwave method[b]			Classical method[c]		Microwave method[b]			Classical method[c]	
Product	Reaction time (min)	Yield (%)	Reaction time (h)	Yield (%)	Product	Reaction time (min)	Yield (%)	Reaction time (h)	Yield (%)
2a	6	78	16	78	**2h**	6	87	16	86
2b	6	95	16	82	**2i**	6	95	16	81
2c	6	90	16	86	**2j**	6	85	16	80
2d	6	90	16	86	**2k**	6	90	16	90
2e	6	95	16	81	**2l**	6	82	16	87
2f	6	91	16	79	**2m**	6	87	8	60
2g	6	85	16	80					

[a] Yields of isolated products.
[b] Reaction conditions: toluene, pyridine, 80°C MW, 45 W.
[c] Reaction conditions: H_2O, pyridine, 35–50°C.
[**2a**, **2b**, **2m**; Refs. 5a and 7a]; methanol, HCl, reflux, [**2k**, **2l**; Ref. 7c and for **2c–j**].

water/pyridine at 35–70°C, with a range of reaction times between 8 and 16 h.[5a,7a,7c]

Considering that microwave irradiation (MW) using commercial domestic ovens has been recently used to accelerate organic reactions, the high heating efficiency giving remarkable rate enhancement and dramatic reduction in reaction times,[20] the aim of this work is to demonstrate the advantages obtained by the use of microwave irradiation in the synthesis of 5-hydroxy-5-trichloromethyl-4,5-dihydroisoxazoles **2a–m** (Scheme 1) using the same precursors of the *classical method*.

The 4-methoxy-1,1,1-trihalo-3-alken-2-ones **1a–m** were synthesized from the reaction of the respective enol ether or acetal with trichloroacetyl chloride.[5,6]

The syntheses of **2a–m** were carried out from the cyclocondensation reaction of **1a–m** with hydroxylamine hydrochloride in a molar ratio of 1:1.2, respectively, in a mixture of toluene and pyridine (1:1) and subjected to microwave irradiation for 6 min at the temperature $\leq$80°C. Table 1 shows the reaction conditions, reaction times and yields used to obtain compounds **2a–m** by *microwave* and *classical methods*.

The present new method of the formation of 5-hydroxy-5-trichloromethyl-4,5-dihydroisoxazoles **2a–m** under microwave irradiation offers several advantages: faster reaction rates, fewer byproducts, high yields, less expensive equipment, while the *classical method* of formation of 4,5-dihydroisoxazoles involves a long tedious process (ca. 16 h). In Table 1 it is possible to observe that the average yields of products obtained by the *microwave method* are ca. 10% higher than those obtained by the *classical method*. The reaction time of the *microwave method* is the main 'goal' of this method in relation to other methods, where the average time ratio between two methods is 1:160 (!).

Unless otherwise indicated, all common reagents and solvents were used as obtained from commercial supplies without further purifications. The melting points were taken on a melting point microscope Reichert–Thermovar and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 400 (^{1}H at 400.13 MHz and ^{13}C at 100.62 MHz) in 5 mm sample tubes at 298 K (digital resolution ±0.01 ppm) in $CDCl_3$/TMS solutions. The CH elemental analyses were performed on an Elemental Analysensysteme Vario EL. Microwave irradiations were conducted in a Panasonic M720 at a frequency of 2450 MHz, with an energy in the sample[21] of 45 W and temperature $\leq$80°C. The selected physical and spectral data for **2a–m** are presented in Ref. 22.

*Synthesis of 5-hydroxy-5-trichloromethyl-4,5-dihydro isoxazoles **2a–k***: (*microwave method*): A mixture of **1** (10 mmol), hydroxylamine hydrochloride (0.84 g, 12 mmol), pyridine (5 mL) and toluene (5 mL) was stirred for a few minutes, then the mixture was irradiated in a microwave oven at 45 W for 6 min, time sufficient to complete the reaction. To the reaction mixture was added a 10% HCl solution (30 mL) and the product was extracted with chloroform (2×20 mL), washed with distilled water (2×30 mL) and dried with $MgSO_4$. The solvent was removed in a rotavapor and the product was obtained in high purity. When necessary the product was recrystallized from cyclohexane.

*Synthesis of 5-hydroxy-5-trichloromethyl-4,5-dihydro isoxazoles **2a–k***: (*classical method*):[7c] A solution of **1** (10 mmol), $NH_2OH{\cdot}HCl$ (0.84 g, 12 mmol), concentrated hydrochloric acid (20.2 mmol), in methanol (30 mL) was stirred under reflux for 16 h. The work-up was carried out as described for the *microwave method*.

Acknowledgements

The authors thank the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq, Contracts No. 46.0804/00-6 and 480067/01-5), Fundação de Amparo à Pesquisa do Estado do Rio Grande do Sul (FAPERGS) and CAPES for financial support and fellowships.

References

1. (a) Manson, A. J.; Stoner, F. W.; Neumann, H. C.; Christiansen, R. G.; Clarke, R. L.; Ackerman, J. H.; Page, D. F.; Dean, J. W.; Phillips, D. K.; Potts, G. O.; Arnold, A.; Beyler, A. L.; Clinton, R. O. *J. Med. Chem.* **1963**, *6*, 1; (b) Lednicer, D.; Mitscher, L. A. *Organic Chemistry of Drugs Synthesis*, Wiley: New York, 1977; Vols. 1–3; (c) De Arriba, A. F.; Gómez-Casajús, L. A.; Cavalcanti, F.; Almansa, C.; García-Rafanell, J.; Forn, J. *Eur. J. Pharmacol.* **1996**, *318*, 341; (d) De Arriba, A. F.; Gómez-Casajús, L. A.; Cavalcanti, F.; Almansa, C.; García-Rafanell, J. *J. Med. Chem.* **1997**, *40*, 547; (e) Harper, R. W.; Jackson, W. T.; Froelich, L. L.; Boyd, R. J.; Aldridge, T. E.; Herron, D. K. *J. Med. Chem.* **1994**, *37*, 2411.
2. (a) Ishii, S.; Yagi, K.; Umehara, T.; Kudo, M.; Nawamaki, T.; Watanabe, S. Japan Kokai, Tokkyo Koho JP 02, 129, 171. *Chem. Abstr.* **1990**, *113* 17201a; (b) Buntain, I. G.; Hatton, L. R.; Hawkins, D. W.; Pearson, C. J.; Roberts, D. A. Eur. Pat. Appl. EP 295, 117. *Chem. Abstr.* **1990**, *112*, 35845n; (c) Moser, H.; Bohner, B.; Foery, W. Eur. Pat. Appl. EP 268, 554; *Chem. Abstr.* **1988**, *110*, 23879; (d) Ishii, T.; Shimotori, H.; Tanaka, Y.; Ishikawa, K. Japan Kokai, Tokkyo Koho JP 01, 168, 675. *Chem. Abstr.* **1989**, *112*, 35854; (e) Okada, I.; Yoshida, K.; Sekine, K. Japan Kokai, Tokkyo Koho, JP 02, 292, 263. *Chem. Abstr.* **1990**, *114*, 185497; (f) Sohn, E.; Handle, R.; Mildenberger, H.; Buerstell, H.; Bauer, K.; Bieringer, H. German Patent 3, 633, 840. *Chem. Abstr.* **1988**, *110*, 8202.
3. (a) Gombos, Z.; Nyitrai, J.; Doleschall, G.; Kolonits, P.; Párkányi, L.; Kálmán, A. *J. Chem. Soc., Perkin Trans. 1* **1993**, 139; (b) Pavarelo, P.; Varasi, M. *Synth. Commun.* **1992**, *22*, 1939; (c) Dannhardt, G.; Kiefer, W.; Lambrecht, G. *Eur. J. Med. Chem.* **1995**, *30*, 839.
4. Lang, S. A., Jr.; Lin, Y.-i. In *Comprehensive Heterocyclic Chemistry*; Katritzky, A. R.; Rees, C. W., Eds. Isoxazoles and their benzo derivatives; Pergamon Press: Oxford, 1984; Vol. 6, pp. 1–130 and references cited therein.
5. (a) Colla, A.; Martins, M. A. P.; Clar, G.; Krimmer, S.; Fischer, P. *Synthesis* **1991**, *6*, 483; (b) Martins, M. A. P.; Zoch, A. N.; Flores, A. F. C.; Clar, G.; Zanatta, N.; Bonacorso, H. G. *J. Heterocycl. Chem.* **1995**, *32*, 739.
6. (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.
7. (a) Martins, M. A. P.; Flores, A. C.; Freitag, R.; Zanatta, N. *J. Heterocycl. Chem.* **1995**, *32*, 731; (b) Martins, M. A. P.; Flores, A. C.; Freitag, R. A.; Zanatta, N. *J. Heterocycl. Chem.* **1996**, *33*, 1223; (c) Martins, M. A. P.; Siqueira, G. M.; Bastos, G. P.; Bonacorso, H. G.; Zanatta, N. *J. Heterocycl. Chem.* **1996**, *33*, 1619; (d) Martins, M. A. P.; Flores, A. F. C.; Bastos, G. P.; Zanatta, N.; Bonacorso, H. G. *J. Heterocycl. Chem.* **1999**, *36*, 837; (e) Martins, M. A. P.; Neto, M.; Sinhorin, A. P.; Bastos, G. P.; Zimmermann, N. E. K.; Rosa, A.; Bonacorso, H. G.; Zanatta, N. *Synth. Commun.* **2002**, *32*, 425.
8. Martins, M. A. P.; Sinhorin, A. P.; Zimmermann, N. E. K.; Zanatta, N.; Bonacorso, H. G.; Bastos, G. P. *Synthesis* **2001**, *13*, 1959.
9. (a) Braibante, M. E. F.; Martins, M. A. P.; Clar, G. *J. Heterocycl. Chem.* **1993**, *30*, 1159; (b) Bonacorso, H. G.; Oliveira, M. R.; Wentz, A. P.; Wastowski, A. D.; Oliveira, A. B.; Hörner, M.; Zanatta, N.; Martins, M. A. P. *Tetrahedron* **1999**, *55*, 345.
10. Martins, M. A. P.; Pereira, C. M. P.; Sinhorin, A. P.; Bastos, G. P.; Zimmermann, N. E. K.; Rosa, A.; Bonacorso, H. G.; Zanatta, N. *Synth. Commun.* **2002**, *32*, 419.
11. Zanatta, N.; Rosa, L. S.; Loro, E.; Bonacorso, H. G.; Martins, M. A. P. *J. Fluorine Chem.* **2001**, *107*, 149.
12. (a) Madruga, C. C.; Clerici, E.; Martins, M. A. P.; Zanatta, N. *J. Heterocycl. Chem.* **1995**, *32*, 735; (b) Zanatta, N.; Cortelini, M. F. M.; Carpes, M. J. S.; Bonacorso, H. G.; Martins, M. A. P. *J. Heterocycl. Chem.* **1997**, *34*, 509; (c) Zanatta, N.; Madruga, C. C.; Marisco, P. C.; Flores, D. C.; Bonacorso, H. G.; Martins, M. A. P. *J. Heterocycl. Chem.* **2000**, *37*, 1213; (d) Zanatta, N.; Pacholski, I. L.; Faoro, D.; Bonacorso, H. G.; Martins, M. A. P. *Synth. Commun.* **2001**, *31*, 2855.
13. Zanatta, N.; Barichello, R.; Bonacorso, H. G.; Martins, M. A. P. *Synthesis* **1999**, *5*, 765.
14. Bonacorso, H. G.; Bittencourt, S. R. T.; Lourega, R. V.; Flores, A. F. C.; Zanatta, N.; Martins, M. A. P. *Synthesis* **2000**, 1.
15. (a) Bonacorso, H. G.; Bittencourt, S. R. T.; Wastowski, A. D.; Wentz, A. P.; Zanatta, N.; Martins, M. A. P. *Tetrahedron Lett.* **1996**, *37*, 9155; (b) Bonacorso, H. G.; Bittencourt, S. R. T.; Wastowski, A. D.; Wentz, A. P.; Zanatta, N.; Martins, M. A. P. *J. Heterocycl. Chem.* **1999**, *36*, 45.
16. (a) Nanajdenko, V. G.; Sanin, A. V.; Balenkova, E. S. *Molecules* **1997**, *2*, 186; (b) Schoth, R.-M.; Sevanard, D.; Pashkevich, K.; Röschenthaler, G.-V. *Coord. Chem. Rev.* **2000**, *210*, 101; (c) Lin, P.; Jiang, J. *Tetrahedron* **2000**, *56*, 3635; (d) Singh, R. P.; Shreeve, J. M. *Tetrahedron* **2000**, *56*, 7613.
17. (a) Martins, M. A. P.; Freitag, R. A.; Flores, A. F. C.; Zanatta, N. *Synthesis* **1995**, 1491; (b) Martins, M. A. P.; Freitag, R. A.; Rosa, A.; Flores, A. F. C.; Zanatta, N.; Bonacorso, H. G. *J. Heterocycl. Chem.* **1999**, *36*, 217.
18. Martins, M. A. P.; Flores, A. F. C.; Bastos, G. P.; Sinhorin, A. P.; Bonacorso, H. G.; Zanatta, N. *Tetrahedron Lett.* **2000**, *41*, 293.
19. Spiegler, W.; Götz, N. *Synthesis* **1986**, 69.
20. (a) Lidström, P.; Tierney, J.; Wathey, B.; Westman, J. *Tetrahedron* **2001**, *57*, 9225 and references cited therein; (b) Dandia, A.; Singh, R.; Sachdeva, H.; Arya, K. *J. Fluorine Chem.* **2001**, *111*, 61; (c) Kidwai, M.; Misra, P. *Synth. Commun.* **1999**, *29*, 3237.
21. (a) Kingston, H. M.; Jassie, L. B. *Introduction to Microwave Sample Preparation—Theory and Practice*; ACS: Washington, 1988; (b) Pecoraro, E.; Davolos, M. R.; Jafelicci, M., Jr. *Quimica Nova* **1997**, *20*, 89.
22. All compounds **2a**–**m** were fully characterized by spectroscopy methods.
    Data for **2a**: $C_4H_4Cl_3NO_2$, mw 204.43, mp 101°C, lit.;[5a] ^{1}H NMR δ (J, Hz) 7.49 (s, 1H, H-3), 3.74 (d, 1H, J=18.8, Ha-4), 3.29 (d, 1H, J=18.8, Hb-4); ^{13}C NMR δ 148.5 (C-3), 110.5 (C-5), 102.4 (C-6), 46.2 (C-4); anal. calcd C, 23.50; H, 1.97; found: C, 23.39; H, 1.96%. **2b**: $C_5H_6Cl_3NO_2$, mw 218.46, mp 127°C, lit.;[5a] ^{1}H NMR δ (J, Hz) 3.70 (d, 1H, J=18.8, Ha-4) 3.23 (d, 1H, J=18.8, Hb-4), 2.04 (s, 3H, H-8), 156.7 (C-3), 111.1 (C-5), 101.9 (C-6), 47.9 (C-4); anal. calcd C, 27.49; H, 2.77; found: C, 27.30; H, 2.75%. **2c**: $C_6H_8Cl_3NO_2$, mw 232.49, mp 121–122°C; ^{1}H NMR δ (J, Hz) 3.71 (d, 1H, J=18.6, Ha-4), 3.24 (d, 1H, J=18.6, Ha-4); ^{13}C NMR δ 161.7 (C-3), 111.7

(C-5), 102.7 (C-6), 47.1 (C-4); anal. calcd C, 31.00; H, 3.47; found: C, 30.72; H, 3.44%. **2d**: $C_7H_{10}Cl_3NO_2$, mw 246.51, mp 140–141°C; ^{1}H NMR δ (J, Hz) 3.70 (d, 1H, $J=18.8$, Ha-4), 3.23 (d, 1H, $J=18.8$, Hb-4); ^{13}C NMR δ 160.5 (C-3), 111.6 (C-5), 102.7 (C-6), 47.2 (C-4); anal. calcd C, 34.11; H, 4.09; found: C, 33.93; H, 4.06%. **2e**: $C_7H_{10}Cl_3NO_2$, mw 246.51, mp 139–140°C; ^{1}H NMR δ (J, Hz) 3.69 (d, 1H, $J=18.8$, Ha-4), 3.28 (d, 1H, $J=18.8$, Hb-4); ^{13}C NMR δ 164.7 (C-3), 111.6 (C-5), 102.8 (C-6), 45.3 (C-4); anal. calcd C, 34.11; H, 4.09, found: C, 33.98; H, 4.07%. **2f**: $C_7H_8Cl_3NO_2$, mw 244.50, mp 164–165°C; ^{1}H NMR δ (J, Hz) 3.55 (d, 1H, $J=18.8$, Ha-4), 3.07 (d, 1H, $J=18.8$, Hb-4); ^{13}C NMR δ 162.5 (C-3), 111.6 (C-5), 102.7 (C-6), 45.4 (C-4); anal. calcd C, 34.39; H, 3.30; found: C, 34.16; H, 3.27%. **2g**: $C_8H_{12}Cl_3NO_2$, mw 260.54, mp 115°C; ^{1}H NMR δ (J, Hz) 3.71 (d, 1H, $J=18.8$, Ha-4), 3.23 (d, 1H, $J=18.8$, Hb-4); ^{13}C NMR δ 160.7 (C-3), 111.6 (C-5), 102.7 (C-6), 45.4 (C-4); anal. calcd C, 36.88; H, 4.64; found: C, 39.69; H, 4.62%. **2h**: $C_8H_{12}Cl_3NO_2$, mw 260.54, mp 152–154°C; ^{1}H NMR δ (J, Hz) 3.69 (d, 1H, $J=18.7$, Ha-4), 3.22 (d, 1H, $J=18.7$, Hb-4); ^{13}C NMR δ 160.0 (C-3), 111.6 (C-5), 102.8 (C-6), 47.2 (C-4); anal. calcd C, 36.88; H, 4.64; found: C, 36.71; H, 4.60%. **2i**: $C_8H_{12}Cl_3NO_2$, mw 260.54, mp 170–171°C; ^{1}H NMR δ (J, Hz) 3.73 (d, 1H, $J=18.6$, Ha-4), 3.30 (d, 1H, $J=18.6$, Hb-4); ^{13}C NMR δ 166.9 (C-3), 111.6 (C-5), 102.4 (C-6), 44.4 (C-4); anal. calcd C, 36.88; H, 4.64; found: C, 36.55; H, 4.58%. **2j**: $C_{10}H_{16}Cl_3NO_2$, mw 288.59, mp 86–87°C; ^{1}H NMR δ (J, Hz) 3.69 (d, 1H, $J=18.6$, Ha-4), 3.30 (d, 1H, $J=18.6$, Hb-4); ^{13}C NMR δ 160.7 (C-3), 111.6 (C-5), 102.8 (C-6), 47.4 (C-4); anal. calcd C, 41.62; H, 5.59; found: C, 41.46; H, 5.53%. **2k**, $C_{10}H_8Cl_3NO_2$, mw 280.53, mp 156°C, lit.;[7c] ^{1}H NMR δ (J, Hz) 4.16 (d, 1H, $J=18.8$, Ha-4), 3.73 (d, 1H, $J=18.8$, Hb-4); ^{13}C NMR δ 157.3 (C-3), 112.8 (C-5), 102.5 (C-6), 45.3 (C-4); anal. calcd C, 42.82; H, 2.87; found: C, 42.59; H, 2.85%. **2l**, $C_{10}H_7Cl_3N_2O_4$, mw 325.52, mp 198°C, lit.;[7c] ^{1}H NMR δ (J, Hz) 4.28 (d, 1H, $J=18.8$, Ha-4), 3.83 (d, 1H, $J=18.8$, Hb-4); ^{13}C NMR δ 157.1 (C-3), 113.5 (C-5), 102.0 (C-6), 45.4 (C-4); anal. calcd C, 36.90; H, 2.17; found: C, 36.76; H, 2.14%. **2m**: $C_8H_{10}Cl_3NO_2$, mw 258.52, mp 148–151°C, lit.;[7a] ^{1}H NMR δ (J, Hz) 3.53 (m, 1H, H-4); ^{13}C NMR δ 161.6 (C-3), 110.2 (C-5), 103.5 (C-6), 53.5 (C-4); anal. calcd C, 37.17; H, 3.90; found: C, 39.91; H, 3.86%.