IRANIAN JOURNAL OF CATALYSIS



Rice husk ash (RHA): A Highly efficient solid acid catalyst for the oxidation of alcohols and trimethylsilyl, tetrahydropyranyl and methoxymethyl ethers with CrO₃

Farhad Shirini*, Masoumeh Abedini, Mahnaz Shamsi-Sani, Mohadeseh Seddighi

Department of Chemistry, College of Science, University of Guilan, Rasht, Zip code 41335, I.R. Iran.

Received 22 July 2014; received in revised form 20 October 2014; accepted 22 October 2014

ABSTRACT

A mild, efficient and fast method for the oxidation of alcohols and trimethylsilyl, tetrahydropyranyl and methoxymethyl ethers to their corresponding carbonyl compounds using CrO_3 in the presence of rice husk ash (RHA) is reported. All reactions were performed at room temperature in high to excellent yields. A new, efficient and green catalyst, heterogeneous reaction conditions, easy work-up of the products and high reaction rates are the main advantages of this method.

Keywords: *Rice husk ash; CrO₃; Alcohols; Trimethylsilyl ethers; Tetrahydropyranyl ethers; Methoxymethyl ethers; Oxidation reactions.*

1. Introduction

Aldehydes and ketones are considered as important precursors for the preparation of many of the organic compounds, including valuable fine chemicals, such as fragrances, vitamins and drugs [1]. Oxidation of alcohols and oxidative deprotection of trimethylsilyl, tetrahydropyranyl and methoxymethyl ethers is one of the main methods for the preparation of these compounds and several methods have been explored to such conversions [2-14]. Several reagents for the oxidation of the above mentioned compounds have been reported which of them chromium (VI)-based oxidants impregnated on solid supports have been extensively used in organic synthesis [15-31].

However, some of the reported methods suffer from disadvantages, such as long reaction times, low yields of the products, use of expensive reagents, requirement of the aqueous reaction conditions and tedious workup. Therefore, introduction of an inexpensive and efficient reagent and/ or reagent system for this reaction under milder conditions is still in demand.

In recent years, use of green reagents in organic reactions is attracted the attention of many organic chemists. This attention can be attributed to the reduction of environmental pollution and the cost of

*Corresponding author email: shirini@guilan.ac.ir Tel/Fax: +98 13 3322 6232 applied methods. Rice husk and rice husk ash are two of these types of reagents which are recently used as solid acid catalysts in some of the important organic reactions [32-35].

2. Experimental

Chemicals were purchased from Fluka, Merck and Aldrich Chemical Companies. All the products were separated and characterized using spectral analysis (IR and NMR). All yields refer to the isolated products. The purity determination of the substrate and reaction monitoring were accompanied by TLC on silica-gel polygram SILG/UV 254 plates.

2.1. Catalyst preparation and chemical composition

The rice husk from an Iranian type of rice, named as Hassani, was burned at 600 $^{\circ}$ C for 1 h to obtain appropriate RHA. The X-ray fluorescence (XRF) analysis showed a high value of silica content for the sample (up to 80%). Other composition such as P₂O₅, K₂O, Na₂O, Al₂O₃, Fe₂O₃, SO₃ and CaO are also present in RHA as a very small proportion of metallic elements [35].

2.2. General procedure

A mixture of the substrate (1 mmol), RHA (50 mg) and CrO_3 (70 mg, 0.7 mmol) was thoroughly mixed at room temperature for the specified time. The progress of the reaction was monitored by TLC (*n*-hexane/

EtOAc= 10:2). After completion of the reaction, the mixture was diluted with 5 mL CH_2Cl_2 and filtered. The solid residue was washed with CH_2Cl_2 (3×5 mL). Evaporation of the solvent followed by column chromatography on silica gel gave the corresponding carbonyl compounds in good to high yields.

3. Results and Discussion

In the past decade a considerable part of our research program is focused on the development of new methods and use of new reagents for the oxidation of organic compounds [36-43].

Here in and in continuation of these studies, we wish to report the applicability of rice husk ash (RHA) as solid acid catalyst in the promotion of the oxidation of alcohols and trimethylsilyl, tetrahydropyranyl and methoxymethyl ethers with CrO₃.

At first step and in order to optimize the reaction conditions, oxidation of 2-chlorobenzyl alcohol by CrO₃ in the presence of RHA was studied as a model reaction. The reaction was performed under solventfree conditions, using different amounts of RHA and CrO₃ at room temperature. The results are shown in Table 1. The obtained results showed that the reaction using 50 mg of RHA and 0.7 mmol of CrO₃ in the absence of solvent proceeded in highest yield in very short reaction times (Table 1, entry 5). It is important to note that the reaction in the absence of RHA was not completed even after long times (Table 1, entry 7). On the other hand the results showed that the reaction in the absence of CrO_3 and in the presence of RHA without oxidant was not occurred at all (Table 1, entry 6).

After optimization of the reaction conditions and in order to show the general applicability of this method, different types of alcohols were subjected to the same reaction under the determined conditions (Scheme 1). The results are summarized in Table 2.

Using this method different types of benzylic alcohols are efficiently converted to their corresponding carbonyl compounds in high yields in very short times (Table 2, entries 1-15). Although in most cases the yields of the products are relatively high, in the case of the benzylic alcohols containing nitro group (Table 2, entries 12, 13) or acyclic aliphatic alcohols (Table 2, entries 17-19) the rate of the reaction is very slow and the reaction temperature is very high (100 $^{\circ}$ C). No traces of carboxylic acids or by-products were detected in all the cases studied.

After the successful oxidation of alcohols, we were interested in extending the applicability of the above reagent system to direct oxidation of trimethylsilyl, tetrahydropyranyl and methoxymethyl ethers to their corresponding carbonyl compounds (Scheme 1).

Table 1. Influence of different conditions on the oxidation of 2-chlorobenzyl alcohol with CrO_3 / RHA under solvent-free conditions.

Entry	RHA (mg)	CrO ₃ (mmol)	Time (min) ^a	Conversion (%)	
1	100	1	Immediately	100	
2	50	0.5	Immediately	100	
3	100	0.5	Immediately	100	
4	50	1	Immediately	100	
5	50	0.7	Immediately	100	
6	50		30		
7		0.5	30	50	

^aImmediately means < 2 min.



Scheme 1. Oxidation of alcohols and trimethylsilyl, tetrahydropyranyl and methoxymethyl ethers to their corresponding carbonyl compounds using CrO₃ in the presence of RHA.

Entry	Substrate	Product	Time (min) ^c	Yield (%) ^d
1	C ₆ H ₅ CH ₂ OH	C ₆ H ₅ CHO	Immediately	95
2	2-ClC ₆ H ₄ CH ₂ OH	2-ClC ₆ H ₄ CHO	Immediately	100 (98, 96, 93, 90)
3	4-ClC ₆ H ₄ CH ₂ OH	4-ClC ₆ H ₄ CHO	Immediately	95
4	3,4-Cl ₂ C ₆ H ₃ CH ₂ OH	3,4-Cl ₂ C ₆ H ₃ CHO	Immediately	100
5	2-BrC ₆ H ₄ CH ₂ OH	2-BrC ₆ H ₄ CHO	Immediately	95
6	2-MeC ₆ H ₄ CH ₂ OH	2-MeC ₆ H ₄ CHO	Immediately	100
7	4-Me ₂ CHC ₆ H ₄ CH ₂ OH	4-Me ₂ CHC ₆ H ₄ CHO	Immediately	95
8	4-Me ₃ CC ₆ H ₄ CH ₂ OH	4-Me ₃ CC ₆ H ₄ CHO	Immediately	100
9	3-MeOC ₆ H ₄ CH ₂ OH	3-MeOC ₆ H ₄ CHO	Immediately	95
10	4-MeOC ₆ H ₄ CH ₂ OH	4-MeOC ₆ H ₄ CHO	Immediately	95
11	2-OHC ₆ H ₄ CH ₂ OH	2-OHC ₆ H ₄ CHO	Immediately	100
12	$2\text{-}NO_2C_6H_4CH_2OH$	2-NO ₂ C ₆ H ₄ CHO	23 ^b	80
13	4-NO ₂ C ₆ H ₄ CH ₂ OH	4-NO ₂ C ₆ H ₄ CHO	10 ^b	90
14	Ph ₂ CHOH	Ph ₂ CO	Immediately	95
15	PhCH(OH)Me	PhCOMe	Immediately	95
16	PhCH(OH)COPh	PhCOCOPh	20 ^b	80
17	C ₆ H ₅ CH ₂ CH ₂ OH	C ₆ H ₅ CH ₂ CHO	10 ^b	70
18	C ₆ H ₅ CH ₂ CH ₂ CH ₂ OH	C ₆ H ₅ CH ₂ CH ₂ CHO	5 ^b	90
19	C ₆ H ₅ CH(CH ₃)CH ₂ OH	C ₆ H ₅ CH(CH ₃)CHO	10 ^b	80
20	C ₆ H ₅ CH=CHCH ₂ OH	C ₆ H ₅ CH=CHCHO	10 ^b	70
21	OH OH		Immediately	100
22	СН-ОН	CHO CHO	Immediately	95
23			Immediately	80
24	CH ₂ OH OH	CHO	Immediately	80
25	J OH		Immediately	95

Table 2. Oxidation of alcohols using CrO₃/ RHA reagent system in the absence of solvent^{a,b}.

^aProducts were characterized by their physical constants, comparison with authentic samples and IR and NMR spectroscopy. ^bReactions were performed at 100 °C.

^cImmediately means < 2 min.

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^dYields are based on isolated products.

The obtained results showed that the same reaction conditions can also be efficiently used for the oxidation of various trimethylsilyl, tetrahydropyranyl and methoxymethyl ethers (including aromatic, aliphatic and cyclic ones) in high to excellent yields in very short times as well as alcohols (Tables 3-5).

Tuble 5. Oxidution of timethylonyl ethers using Croy runn reugent system in the desence of solvent

		<u>J</u> - <u>J</u>		
Entry	Substrate	Product	Time (min) ^b	Yield (%) ^c
1	C ₆ H ₅ CH ₂ OSiMe ₃	C ₆ H ₅ CHO	Immediately	100
2	2-ClC ₆ H ₄ CH ₂ OSiMe ₃	2-ClC ₆ H ₄ CHO	Immediately	100
3	4-ClC ₆ H ₄ CH ₂ OSiMe ₃	4-ClC ₆ H ₄ CHO	Immediately	100 (98, 97, 94, 92 ^d)
4	3,4-Cl ₂ C ₆ H ₃ CH ₂ OSiMe ₃	3,4-Cl ₂ C ₆ H ₃ CHO	Immediately	100
5	2-BrC ₆ H ₄ CH ₂ OSiMe ₃	2-BrC ₆ H ₄ CHO	Immediately	100
6	2-MeC ₆ H ₄ CH ₂ OSiMe ₃	2-MeC ₆ H ₄ CHO	Immediately	95
7	4-Me ₂ CHC ₆ H ₄ CH ₂ OSiMe ₃	4-Me ₂ CHC ₆ H ₄ CHO	Immediately	100
8	4-Me ₃ CC ₆ H ₄ CH ₂ OSiMe ₃	4-Me ₃ CC ₆ H ₄ CHO	Immediately	100
9	3-MeOC ₆ H ₄ CH ₂ OSiMe ₃	3-MeOC ₆ H ₄ CHO	Immediately	100
10	4-MeOC ₆ H ₄ CH ₂ OSiMe ₃	4-MeOC ₆ H ₄ CHO	Immediately	100
11	2-OHC ₆ H ₄ CH ₂ OSiMe ₃	2-OHC ₆ H ₄ CHO	Immediately	100
12	$2-NO_2C_6H_4CH_2OSiMe_3$	2-NO ₂ C ₆ H ₄ CHO	Immediately	100
13	4-NO ₂ C ₆ H ₄ CH ₂ OSiMe ₃	4-NO ₂ C ₆ H ₄ CHO	Immediately	90
14	Ph ₂ CHOSiMe ₃	Ph ₂ CO	Immediately	100
15	PhCH(OSiMe ₃)Me	PhCOMe	Immediately	100
16	PhCH(OSiMe ₃)COPh	PhCOCOPh	Immediately	100
17	C ₆ H ₅ CH ₂ CH ₂ OSiMe ₃	C ₆ H ₅ CH ₂ CHO	Immediately	100
18	$C_6H_5CH_2CH_2CH_2OSiMe_3$	C ₆ H ₅ CH ₂ CH ₂ CHO	Immediately	100
19	C ₆ H ₅ CH(CH ₃)CH ₂ OSiMe ₃	C ₆ H ₅ CH(CH ₃)CHO	Immediately	100
20	C ₆ H ₅ CH(OSiMe ₃)CH ₂ CH ₃	C ₆ H ₅ COCH ₂ CH ₃	Immediately	100
21	C ₆ H ₅ CH=CHCH ₂ OSiMe ₃	C ₆ H ₅ CH=CHCHO	Immediately	70
22	OSiMe ₃	o L	T 11 , 1	100
22	\bigcirc	\bigcirc	Immediately	100
23	CH ₂ OSiMe ₃	CHO	Immediately	100
24	OSiMe ₃		Immediately	100
25	OSiMe ₃	<u>ر ا</u>	Immediately	100
26	OSiMe ₃		Immediately	100
27	C ₆ H ₅ CH ₂ NHCH ₂ CH ₂ OSiMe ₃	C ₆ H ₅ CH ₂ NHCH ₂ CHO	Immediately	100

^aProducts were characterized by their physical constants, comparison with authentic samples and IR and NMR spectroscopy.

^bImmediately means < 2 min.

^cYields are based on isolated products.

^d5 min.

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Entry	Substrate	Product	Time (min) ^b	Yield (%) ^c
1	C ₆ H ₅ CH ₂ OTHP	C ₆ H ₅ CHO	Immediately	100
2	2-ClC ₆ H ₄ CH ₂ OTHP	2-ClC ₆ H ₄ CHO	Immediately	100
3	4-ClC ₆ H ₄ CH ₂ OTHP	4-ClC ₆ H ₄ CHO	Immediately	100
4	3,4-Cl ₂ C ₆ H ₃ CH ₂ OTHP	3,4-Cl ₂ C ₆ H ₃ CHO	Immediately	100
5	2-BrC ₆ H ₄ CH ₂ OTHP	2-BrC ₆ H ₄ CHO	Immediately	100 (98, 95, 94, 90 ^d)
6	2-MeC ₆ H ₄ CH ₂ OTHP	2-MeC ₆ H ₄ CHO	Immediately	95
7	4-Me ₂ CHC ₆ H ₄ CH ₂ OTHP	4-Me ₂ CHC ₆ H ₄ CHO	Immediately	100
8	4-Me ₃ CC ₆ H ₄ CH ₂ OTHP	4-Me ₃ CC ₆ H ₄ CHO	Immediately	100
9	3-MeOC ₆ H ₄ CH ₂ OTHP	3-MeOC ₆ H ₄ CHO	Immediately	100
10	4-MeOC ₆ H ₄ CH ₂ OTHP	4-MeOC ₆ H ₄ CHO	Immediately	100
11	2-OHC ₆ H ₄ CH ₂ OTHP	2-OHC ₆ H ₄ CHO	Immediately	100
12	2-NO ₂ C ₆ H ₄ CH ₂ OTHP	2-NO ₂ C ₆ H ₄ CHO	Immediately	100
13	4-NO ₂ C ₆ H ₄ CH ₂ OTHP	4-NO ₂ C ₆ H ₄ CHO	Immediately	90
14	Ph ₂ CHOTHP	Ph ₂ CO	Immediately	100
15	PhCH(OTHP)Me	PhCOMe	Immediately	100
16	PhCH(OTHP)COPh	PhCOCOPh	Immediately	80
17	C ₆ H ₅ CH ₂ CH ₂ OTHP	C ₆ H ₅ CH ₂ CHO	Immediately	100
18	C ₆ H ₅ CH ₂ CH ₂ CH ₂ OTHP	C ₆ H ₅ CH ₂ CH ₂ CHO	Immediately	100
19	C ₆ H ₅ CH(CH ₃)CH ₂ OTHP	C ₆ H ₅ CH(CH ₃)CHO	Immediately	100
20	C ₆ H ₅ CH(OTHP)CH ₂ CH ₃	C ₆ H ₅ COCH ₂ CH ₃	Immediately	90
21	C ₆ H ₅ CH=CHCH ₂ OTHP	C ₆ H ₅ CH=CHCHO	Immediately	100
22	OTHP		Immediately	100
23	OTHP	CHO	Immediately	90
24	OTHP OTHP		Immediately	100
25	OTHP		Immediately	100
26	OTHP		Immediately	95
27	C ₆ H ₅ CH ₂ NHCH ₂ CH ₂ OTHP	C ₆ H ₅ CH ₂ NHCH ₂ CHO	Immediately	100

Table 4. Oxidation of tetrahydropyranyl	ethers using CrO ₃ / RHA reagent system in t	he absence of solvent ^a .
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^aProducts were characterized by their physical constants, comparison with authentic samples and IR and NMR spectroscopy. ^bImmediately means < 2 min.

^cYields are based on isolated products.

^d 4 min.	
Table 5. Oxidation of methoxymethyl ethers using CrO ₃ / RHA reagent sys	tem in the absence of solvent ^a

Entry	Substrate	Product	Time (min) ^b	Yield (%) ^c
1	C ₆ H ₅ CH ₂ OMOM	C ₆ H ₅ CHO	Immediately	100
2	2-ClC ₆ H ₄ CH ₂ OMOM	2-ClC ₆ H ₄ CHO	Immediately	100
3	4-ClC ₆ H ₄ CH ₂ OMOM	4-ClC ₆ H ₄ CHO	Immediately	100 (98, 97, 93 ^d , 90 ^e)
4	3,4-Cl ₂ C ₆ H ₃ CH ₂ OMOM	3,4-Cl ₂ C ₆ H ₃ CHO	Immediately	100
5	2-BrC ₆ H ₄ CH ₂ OMOM	2-BrC ₆ H ₄ CHO	Immediately	100
6	2-MeC ₆ H ₄ CH ₂ OMOM	2-MeC ₆ H ₄ CHO	Immediately	100
7	4-Me ₂ CHC ₆ H ₄ CH ₂ OMOM	4-Me ₂ CHC ₆ H ₄ CHO	Immediately	100
8	4-Me ₃ CC ₆ H ₄ CH ₂ OMOM	4-Me ₃ CC ₆ H ₄ CHO	Immediately	100
9	3-MeOC ₆ H ₄ CH ₂ OMOM	3-MeOC ₆ H ₄ CHO	Immediately	100
10	4-MeOC ₆ H ₄ CH ₂ OMOM	4-MeOC ₆ H ₄ CHO	Immediately	100
11	2-OHC ₆ H ₄ CH ₂ OMOM	2-OHC ₆ H ₄ CHO	Immediately	100
12	2-NO ₂ C ₆ H ₄ CH ₂ OMOM	2-NO ₂ C ₆ H ₄ CHO	Immediately	100
13	4-NO ₂ C ₆ H ₄ CH ₂ OMOM	4-NO ₂ C ₆ H ₄ CHO	Immediately	90
14	Ph ₂ CHOMOM	Ph ₂ CO	Immediately	100
15	PhCH(OMOM)Me	PhCOMe	Immediately	100
16	PhCH(OMOM)COPh	PhCOCOPh	Immediately	90
17	C ₆ H ₅ CH ₂ CH ₂ OMOM	C ₆ H ₅ CH ₂ CHO	Immediately	100
18	C ₆ H ₅ CH ₂ CH ₂ CH ₂ OMOM	C ₆ H ₅ CH ₂ CH ₂ CHO	Immediately	100
19	C ₆ H ₅ CH(CH ₃)CH ₂ OMOM	C ₆ H ₅ CH(CH ₃)CHO	Immediately	100
20	C ₆ H ₅ CH(OMOM)CH ₂ CH ₃	C ₆ H ₅ COCH ₂ CH ₃	Immediately	90
21	C ₆ H ₅ CH=CHCH ₂ OMOM	C ₆ H ₅ CH=CHCHO	Immediately	100
22	Омом	○ →o	5	90
23	CH ₂ OMOM OMOM	CHO	10	90
24	OMOM	↓ ↓ °	Immediately	100
25	ОМОМ		Immediately	100
26	ОМОМ		3	95
27	C ₆ H ₅ CH ₂ NHCH ₂ CH ₂ OMOM	C ₆ H ₅ CH ₂ NHCH ₂ CHO	Immediately	100

^aProducts were characterized by their physical constants, comparison with authentic samples and IR and NMR spectroscopy. ^bImmediately means < 2 min.

^cYields are based on isolated products.

^d5 min.

^e8 min.

RHA can be easily recovered by filtration, washing with CH_2Cl_2 , H_2O and acetone and drying at room temperature. Our investigations showed that RHA is a reusable catalyst in all types of the oxidation reactions but slight decrease in the yields of the products and slight increase in the times of the reactions was observed after 5 cycles.

To show the efficiency of the selected method, Table 6 compares the results obtained in the present study with some of those reported in the literature.

It is important to note that, this oxidizing reagent system is more effective than the other oxidizing systems with respect to the amounts of the oxidizing agent, reaction times and yields. In addition, in some of the reported methods larger amounts of the catalyst and oxidant are needed while the present method is performed using much lesser amounts of both of CrO_3 and RHA under the grinding conditions.

4. Conclusions

In conclusion, we have introduced a mild, efficient and high yielding method for the oxidation of alcohols and trimethylsilyl, tetrahydropyranyl and methoxymethyl ethers using CrO_3 in the presence of RHA as an efficient oxidizing reagent system. A new, efficient and green catalyst, simple procedure and easy work-up, high reaction rates and excellent yields of the products are among the other advantages of this method, which make this procedure a useful and attractive addition to the available methods.

Table 6. Comparison of our results with some of those reported in the literature.

Entry	Reaction conditions	Time (min)	Yield (%)	Ref.
1	Benzyltriphenylphosphonium chlorate / AlCl ₃ (1 mmol: 0.2 mmol), CH ₃ CN, reflux	0.25-10 h	20-100	[7] ^b
2	CrO ₃ /Al ₂ O ₃ (2 mmol: 2 g), Solvent-free, Grinding	5-10	68-95	[27] ^a
3	(NH ₄) ₂ Cr ₂ O ₇ /Silica chloride (1 mmol: 0.3 g), wet SiO ₂ (0.2 g), Solvent-free, 80 °C	3-30	80-92	[36] ^a
4	Fe(NO ₃) ₃ .9 H ₂ O/ KBr (2 mmol: 0.042 g), CH ₃ CN, reflux	0.67-3.3 h	30-95	[39] ^a
5	Fe(NO ₃) ₃ .9 H ₂ O/ KBr (2 mmol: 0.042 g), CH ₃ CN, reflux	0.25-3.3 h	30-92	[39] ^b
6	HIO ₃ / NaHSO ₄ .H ₂ O (1.5 mmol: 0.035 g), CH ₃ CN, reflux	0.17-6.3 h	70-95	[41] ^b
7	Trinitratocerium(IV) bromate/ NaHSO ₄ .H ₂ O (0.5 mmol: 0.3 g), Solvent-free, r.t.	2-20	82-95	[40] ^b
8	HIO ₄ / Poly(1,4-phenylene-2,5-pyridinedicarboxyamide) (1.05 mmol: 0.6 g), CH ₃ CN, reflux	1-6 h	5-98	[44] ^a
9	CrO ₃ / Silica sulfuric acid (1.25 mmol: 0.25 g), wet SiO ₂ (0.5 g), CH ₃ CN, r.t.	1-30	85-90	[45] ^a
10	CrO ₃ / Silica sulfuric acid (1.25 mmol: 0.25 g), wet SiO ₂ (0.5 g), CH ₃ CN, r.t.	1-90	82-95	[45] ^b
11	CrO ₃ / SANM (1.25 mmol: 0.1 g), Solvent-free, Grinding	2-31	80-98	[46] ^a
12	CrO ₃ / SANM (1.25 mmol: 0.1 g), Solvent-free, Grinding	0.5-9	95-98	[46] ^b
13	CrO ₃ / RHA (0.7 mmol: 0.05 g), Solvent-free, Grinding	Immediately-23	70-100	This work ^a
14	CrO ₃ / RHA (0.7 mmol: 0.05 g), Solvent-free, Grinding	Immediately	70-100	This work ^b

^aOxidation of alcohols.

^bOxidation of silyl and THP ethers.

Acknowledgements

We are thankful to the University of Guilan Research Council for the partial support of this work.

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