Derivatives of Dihydropyrazine-1,4Dioxide, 3Imidazoline 3Oxide, and α-Phenyl Nitrones with Functional Groups as New Spin Traps in Solution and in the Gas Phase

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Derivatives of Dihydropyrazine-1,4-Dioxide, 3-Imidazoline 3-Oxide, and α-Phenyl Nitrones with Functional Groups as New Spin Traps in Solution and in the Gas Phase

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The title compounds, acyclic phenyl nitrones with functional groups, cyclic dinitrones with conjugated or isolated double bonds, and imidazoline nitrones are studied as spin traps (ST) for short-lived free radicals (R) generated photochemically in solution and in the gas phase. New STs are efficient in trapping OH, hydroxyalkyl, or HO_2 radicals. EPR spectra of the spin adducts (SA) of studied dinitrones are triplets of doublets characteristic of the nitroxides with one radical center. Imidazoline ST with amino nitrogen exhibits pH-dependent hyperfine splittings of its SAs. Some spin traps were shown to be efficient in detecting R in the atmospheric experiments.

Introduction

Spin trapping has been widely used to detect and identify short-lived free radicals (R) that cannot be observed directly by EPR because of low concentrations or rapid spin relaxation.[1] The major fields of the application of spin trapping are biochemistry[2] and physical organic chemistry.[1,3] Employment of this method in the detection of free radicals in the gas phase and in the atmosphere is less known.[4] As preliminary tests show, commonly used spin traps have some deficiencies limiting their use for these applications. For example, the efficiency of PBN (α-phenyl-*N-tert*-butyl nitrone) in trapping radicals from the gas phase is rather low. 4-POBN (α-(1-oxide pyridyl-4)-*N-tert*-butyl nitrone), though an efficient spin trap, is easily hydrolyzed, and its spin adducts are not stable.[5] Many spin traps give a background triplet EPR signal that is superposed on the spectra of spin adducts. One more problem is associated with trapping HO_2 radical, since its rate of addition to a spin trap is low and/or lifetimes of its spin adducts are short. For the purpose of elevating the sensitivity of spin traps to different R and the stability of their spin adducts, modifications of the nitrone structure have been proposed, particularly, the creation of steric hindrance to hamper oxidation.[1]

In the present work we describe spin-trapping properties of some new nitrones differing in structure, namely, acyclic α-phenyl nitrones with functional groups, cyclic dinitrones with isolated or conjugated double bonds, and imidazoline derivatives. The variety of structures creates possibilities of choosing a spin trap best suited to a system under investigation (for solubility, selectivity, etc.). In particular, this can help bond a spin trap chemically to a filter for sampling from the gas phase. Some of the new spin traps may be useful for atmospheric chemistry supplements.

Experimental Section

Synthesis. Nitrones (**1**−**19**) were synthesized according to the following methods that were described in detail elsewhere. α-Phenyl nitrones (**1**, **3**, and **4**) were obtained by the condensation of the corresponding α-hydroxylamino ketones or α-hydroxylamino oxime with benzaldehyde.[6,7] α-Phenyl nitrone (**2**) was obtained by the reaction of phenyl vinyl ketone with *anti*-benzaldoxime.[8] 2,5-Dihydropyrazine 1,4-dioxide (**5**) was synthesized by heating α-hydroxylamino oxime in acetone in the

presence of an acid.[9] 3-Imidazoline 3-oxides (**16**, **18**, and **19**) were obtained by condensation of the corresponding α-hydroxylamino oximes or α-amino oximes with benzaldehyde, acetone, or its diethyl ketal.[6,10,11] 1,2,2,5,5-Pentamethyl-3-imidazoline 3-oxide (**17**) was prepared by decarboxylation of 4-carboxy-1,2,2,5,5-pentamethyl-3-imidazoline 3-oxide.[12] 3-Hydroxy-2,3-dihydropyrazine 1,4-dioxides (**6**−**9**) and 4*a*-hydroxyhexahydroquinoxaline 1,4-dioxides (**12** and **13**) were obtained by the condensation of the corresponding α-hydroxylamino oximes with glyoxal, methyl glyoxal, phenyl glyoxal, and diacetyl.[6,13] 2,3-Dihydropyrazine 1,4-dioxide (**10**) and hexahydroquinoxaline 1,4-dioxides (**14** and **15**) were obtained by the condensation of 1,2-bis(hydroxylamines) with glyoxal, phenyl glyoxal, and diacetyl.[14] 2,3- Dihydropyrazine 1,4-dioxide (**11**) was prepared by oxidation of 1,4-dihydroxy-2,2-dimethylpiperazine.[13]

UV Absorption Spectra. UV absorption spectra of the nitrones (**1**−**19**) in ethanol are characterized by the following values of λ_{max} in nm (log ϵ(L/mol cm): **1**−**4**, 294−299 (4.29−4.42); **5**, **16**−**19**, 230−236 (3.95−4.22); **6**−**8**, **10**−**12**, **15**, 345−359 (4.14−4.29); **9**, **13**, **14**, 364−372 (4.05−4.11), 272−275 (4.30−4.35).

Aqueous solutions of the nitrones (0.01−0.05 M) were prepared for spin-trapping experiments. The nitrones were tested as spin traps in standard photochemical systems of R generation: •OH (1% H_2O_2, $h\nu$[15]); 30 mM $K_2S_2O_8$, $h\nu$[16]; HO_2• (10% H_2O_2, $h\nu$[15]); •CH_2OH (1% H_2O_2, 10% CH_3OH, $h\nu$[2]); •C_2H_4OH (1% H_2O_2, 10−30% C_2H_5OH, $h\nu$[2]). The trapping reaction can be shown as

$$-HC=N \rightarrow O + R \rightarrow -HCR-N-O•$$
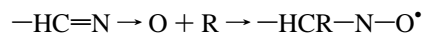
A high-pressure Hg lamp equipped with a glass filter to avoid the photolysis of the nitrone was used for the generation of R. To obtain R in the gas phase, the vapor of a photochemically active compound (H_2O_2, acetone, formaldehyde, acetaldehyde) was photolyzed in the flow of Ar, then blown through the filter with a spin trap deposited on it. The study of trapping properties of the nitrones under atmospheric conditions included high-volume air sampling at a rate of 0.5−0.24 L/min for 10 min to 3 h through a filter with a spin trap.

The pH dependence of spin trapping for the nitrone (**17**) was investigated using standard buffer solutions or adding HCl or NaOH in the pH range 2.3−9.6.
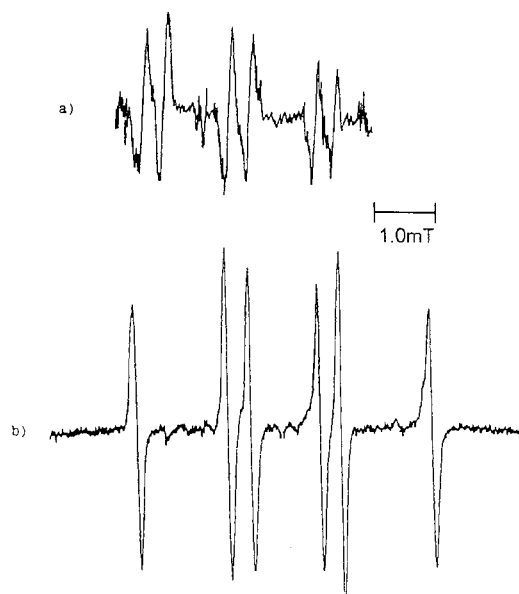
Figure 1. EPR signal of the spin adduct of acyclic spin trap **4**: (a) OH adduct (in a solution containing 0.02 M of nitrone **4** and 1% H_2O_2 in water, irradiated with a high-pressure mercury lamp for 10 s) at a modulation amplitude of 0.08 mT and a receiver gain of 4×10^5; (b) signal appearing simultaneously in the presence of 10% H_2O_2 without irradiation, with 0.02 M **4**, and with a modulation amplitude of 0.08 mT and receiver gain of 1×10^5.

EPR spectra of spin adducts were recorded with a Bruker ER- 200 D-SRC spectrometer in a standard quartz cell. The stability of the magnetic field was 2 mT/h. The microwave power was not higher than 10 mW, and the modulation amplitude was 0.05−0.12 mT. Microwave frequency was 100 kHz and the receiver gain 1×10^4 to 5×10^5. The time constant was 0.2 s, and the scan rate was 10 mT/200 s. The instrumental error of measuring the constants of superfine splitting was 0.004 mT. The *g*-factor was measured relative to an irradiated *n*LiF−Li standard ($g = 2.002\,29$) with the accuracy of 0.0001. Quantitative measurements were carried out by the comparison of the overall intensity of EPR signals of SA with that of the solutions of the stable free radical 2,2,6,6-tetramethyl-4-piperidon-1-oxyl in water and benzene.[17]

Lifetimes τ of spin adducts were determined from the linear dependence of ln *h* (where *h* is the intensity of the first weak-field component of the EPR signal) on the time needed for the 50% decrease of the initial level.

Possible influence of the traces of metal ions on the formation of radical products was checked in experiments with the solutions prepared from deionized water and with the use of ethylenediaminetetraacetic acid (EDTA) as the reagent to chelate the ions.

Results and Discussion

1. Acyclic α-Phenyl Nitrones. Acyclic nitrones (**1−4**) are

(1) (2) (3) (4)
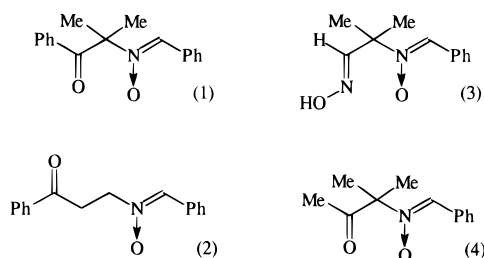
similar to a widely used spin trap PBN but have additional functional groups (keto or oxime) in the alkyl fragment. An example of the EPR spectrum of acyclic spin adducts is shown

in Figure 1. The characteristics of EPR spectra of spin adducts of the acyclic spin traps (**1−4**) are listed in Table 1. The values of a_H are in the range 0.3−0.4 mT, which is typical for acyclic spin adducts and close to those of PBN.[2] The overall intensity of EPR signals of the spin adducts of **1−4** was 2−3 times higher than that of PBN adducts in identical conditions.

The attempts to register adducts of the nitrones (**1−4**) with the HO_2 radical have failed. It was found that in a solution of 10% H_2O_2, as well as in the presence of $K_2S_2O_8$ (30 mM), MnO_2, or PbO_2, the nitrones **3** and **4** form free radicals without irradiation, and the EPR spectra with large a_H values appear. Compound **3** gives rise to a spectrum with $a_N = 1.45$ mT, $a_H = 1.93$ mT. Compound **4** gives $a_N = 1.55$ mT, $a_H = 1.92$ mT. Note that high values of a_H are characteristic of cyclic spin adducts.[2] It is believed that the formation of a nitroxide from compound **3** according to the following scheme can be the reason for this fact:

(3)
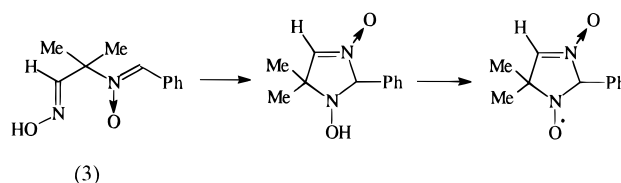
Thus, examination of new nitrones **1−4** shows that they are efficient spin traps of the CH_2OH radical. Only compound **4** can be used for trapping the OH radical. Comparison with PBN suggests that the introduction of substituents is responsible for the loss of OH trapping ability of compounds **1−3**.

2. Pyrazine Derivatives. *(a) 2,2,5,5-Tetramethyl-2,5-dihidropyrazine 1,4-Dioxide (5, DPDO).* DPDO is a six-mem-


(5)
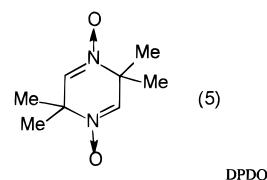
DPDO

bered heterocyclic compound with two nitrone groups. The a_H values for OH and CH_2OH adducts (Table 2) are large and are in the range characteristic of cyclic spin adducts.[2]

DPDO possesses two vacancies for the addition of R, but only the adducts with one radical center were identified. We did not observe the formation of a biradical adduct. Measurements revealed that only 0.01−0.1% of DPDO transformed into spin adducts. So the probability of R addition to nitrone is statistically higher than the addition to a one-centered spin adduct.

Sometimes a background triplet signal appeared in the solutions of DPDO, which was easily removed by passing the solutions of DPDO through a column filled with activated carbon before use.

(b) Conjugated Cyclic Dinitrones. Compounds **6−11** are 2,3-
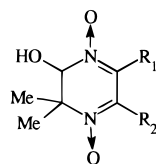
(6) $R_1 = R_2 = Me$
(7) $R_1 = R_2 = H$
(8) $R_1 = Me$, $R_2 = H$
(9) $R_1 = Ph$, $R_2 = H$
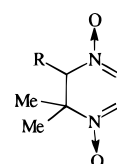
(10) R=Ph
(11) R=H

dihydropyrazine 1,4-dioxides with conjugated nitrone groups.

Spin Traps

J. Phys. Chem., Vol. 100, No. 44, 1996 **17525**

TABLE 1: EPR Parameters of Spin Adducts of Nitrones 1−4

nitrone	CH$_2$OH adduct				OH adduct			
	a_N, mT	a_H, mT	g	τ, min	a_N, mT	a_H, mT	g	τ, min
1	1.54	0.32	2.0057	17	not observed	not observed		
2	1.49	0.36	2.0059	21	not observed	not observed		
3	1.57	0.39	2.0051	27	not observed	not observed		
4	1.51	0.39	2.0057	25	1.50	0.33	2.0057	27
PBN	1.45	0.35	2.0059	21	1.53	0.25	2.0059	35

TABLE 2: EPR Parameters of DPDO Spin Adduct

R	a_N, mT	a_H, mT	g	τ, min
OH	1.55	2.16	2.0058	63
CH$_2$OH	1.57	1.82	2.0059	30

An example of the EPR spectrum is shown in Figure 2, and the results of EPR studies of **6−11** are presented in Table 3.

Despite the presence of two nitrone groups in a molecule, compounds **6−11** formed adducts with one radical center, like in the case with DPDO. It is important to note that the changes in nitrone structure can lead to substantial changes in a_H values of the corresponding spin adducts with one and the same R. Besides, the presence of different substituents in positions 2 and 3 of the heterocycle of compounds **6** and **7** helped to determine that R adds to position 6 in both compounds. Otherwise, the types of EPR spectra of adducts would be different.
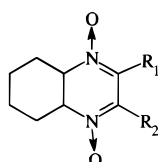
Compound **7** was able to trap also the HO$_2$ radical, and the lifetime of this adduct was 3 min. One of the merits of compounds **6−11** was the absence of background triplet signal.

(c) Hexahydroquinoxaline 1,4-Dioxides. EPR parameters of the spin adducts of dinitrones **12−15** are listed in Table 4. It
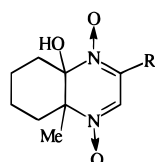

(12) R=Me
(13) R=Ph

(14) R$_1$=H, R$_2$=Ph
(15) R$_1$=R$_2$=Me

can be seen that the values of a_H are characteristic of the cyclic spin adducts.[18]

The occurrence of additional EPR signal with small values of a_H (0.29 mT) in the solution of compound **12** and the growth of the intensity of this signal without irradiation suggest that the reason may be the opening of the cycle.

Lifetimes of the spin adducts of the nitrones **12−15** in solution are sufficient for use of these nitrones as spin traps.
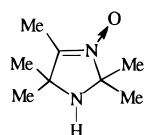
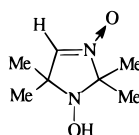**3. Imidazoline Derivatives.** Compound **16** is an efficient
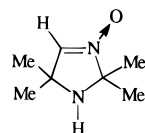
(16)
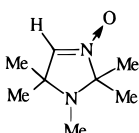
(17)   PMIO

(18)

(19)

spin trap for the OH radical. The values for spin adducts of

OH with **16** are $a_N = 1.49$ mT, $a_H = 1.75$ mT, $g = 2.0056$, $\tau = 41$ min. The values for the adducts of **17** are listed in Table 5.

It was found that a_H values of the spin adducts of PMIO were sharply different in neutral and acidic pH regions. In neutral solutions these a_H values are characteristic of cyclic spin adducts. Transformation of the spectra with changing acidity of the solution is reversible. Earlier, we have shown that the ratio of the intensities of H$^+$−PMIO−R and PMIO−R EPR signals depends on pH.[19] The pK_a was found to be 2.8 for the adduct with OH and 3.3 for the adduct with CH$_2$OH. This result is in agreement with the data on the titration of PMIO solutions with HCl. The values of the corresponding pK_a (2.8 in water and 3.3 in the mixture of water and methanol) were essentially the same as in EPR measurements. The identity of pK_a values for the spin trap and its adducts points to the protonation of the same group, amino nitrogen, as we believe, in nitrone and its adduct. The examples of the pH dependence of EPR spectra of spin adducts are known,[18] but the influence of protonation of a group remote from the radical center on the EPR signal was found for the first time.

The rate constant (k) of OH trapping with PMIO was determined from the time-dependent ratio of signal intensities in competition with PBN ($k_{(PBN−OH)} = 1.9 \times 10^9$ L/mol cm (ref 2)). The value $k_{(PMIO−OH)}$ was measured to be 6.3×10^9 L/mol cm. Protonation caused a decrease of the spin trapping rate by 20−30%.

PMIO was also an efficient spin trap for the HO$_2$ radical. An intensive signal of the PMIO−HO$_2$ adduct was obtained. The lifetime of the PMIO−HO$_2$ adduct is about 8 min, which is the longest compared to the τ of known HO$_2$ adducts (PBN, 2 min; DMPO, ~1 min[2,18]).

The elevated stability of PMIO and its adducts may be due to a high degree of methylation, which creates steric hindrance and hampers oxidation. The presence of amino nitrogen lends to PMIO with a stability in acidic medium that is higher than what other cyclic spin traps exhibit. Protonation of the amino nitrogen causes the observed changes in EPR spectra of spin adducts in acid. The role of amino nitrogen in increasing the stability can be illustrated by the fact that when the hydroxyl-amino group is present, instead of amino in the 1 position of the heterocycle (compounds **18** and **19**), the stability of the nitrone sharply decreases. Thus, compounds **18** and **19** gave triplet EPR signals in aqueous solutions without UV irradiation. Preliminary removal of the dissolved oxygen inhibited the appearance of these signals, which suggested that these compounds should be studied in anaerobic conditions. Neither OH nor CH$_2$OH adducts were observed with compounds **18** and **19**.

Spin Trapping of the Gas Phase Free Radicals. Spin trapping of R from the gas phase requires an elevated efficiency of spin traps and their stability under the sampling conditions. It was found that nitrones **4**, **5**, **8**, and **17** were efficient in trapping the gas phase OH radical. Splitting constants of their spin adducts were the same as those observed after the photolysis of 1% H$_2$O$_2$ solution in the presence of the same spin trap.

The imidazoline spin trap PMIO (**17**) was found to be the most efficient for trapping OH from the gas phase. Organic R

TABLE 3: EPR Parameters of Spin Adducts of Nitrones 6−11

	OH adduct			CH$_2$OH adduct		
nitrone	a_N, mT	a_H, mT	τ, min	a_N, mT	a_H, mT	τ, min
6	1.50		27	1.46		29
7	1.53	1.83	17	1.70	2.00	11
8	1.54	1.99	47	1.53	1.12	41
9	1.54	0.93	58	1.51	0.92	42
10[a]	not observed	not observed		1.65	1.65; 0.41	48
11	1.56	1.01	9	not observed	not observed	

[a] Adduct with hydroxyethyl radical.

TABLE 4: EPR Parameters of Spin Adducts of Nitrones 12−15

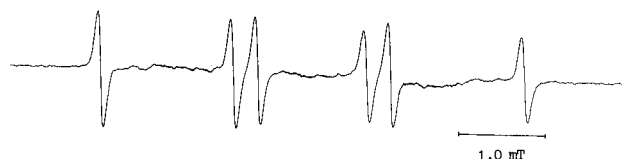|	OH adduct			C$_2$H$_4$OH adduct		
nitrone	a_N, mT	a_H, mT	τ, min	a_N, mT	a_H, mT	τ, min
12	1.55	1.87	32	not observed	not observed	
	1.44[a]	0.29[a]				
13	not observed	not observed		1.47	1.97	34
14	not observed	not observed		1.65	1.12	7
15	1.49	2.48	26	1.53	1.17	18

[a] Appears in the presence of the oxidizer.

Figure 2. EPR signal of the OH adduct of cyclic spin trap **7** (0.02 M **7**, 1% H$_2$O$_2$, irradiated with mercury lamp for 10 s). Modulation amplitude was 0.08 mT, and the receiver gain was 5×10^4.

TABLE 5: EPR Parameters of Spin Adducts of Nitrone 17 (PMIO)

	pH > 3			pH < 4		
R	a_N, mT	a_H, mT	g	a_N, mT	a_H, mT	g
OH	1.46	1.72	2.0056	1.38	0.45	2.0059
OD	1.57	1.93	2.0058	1.36	0.45	2.0059
O$_2^-$/HO$_2$	1.33	0.75	2.0056	1.19	0.85	
CH$_2$OH	1.52	2.25	2.0055	1.39	1.39	2.0057
CD$_2$OD	1.51	2.26	2.0053	1.38	1.38	2.0057
SO$_4^{\bullet-}$	1.33	0.80				

from the gas phase were successfully trapped by nitrones **3−5** and **17**. This was shown for the photolysis of carbonyl compounds (acetone, formaldehyde, or acetaldehyde) as an example.

EPR characteristics of spin adducts with gas phase radicals were shown to depend on the formation conditions. Thus, bubbling through the solutions of spin traps enabled us to observe the formation of adducts, but their lifetimes were shorter than those for spin adducts formed on filters. Spin adducts could be kept on dry paper filters for 2−3 days before washing, and on glass fiber filters this period was as long as a week. Glass fiber filters could be used for compounds **3−5** and **8** but not for **17**. Paper filters were better in the case of **17**.

Since the concentration of R in the atmosphere is $10^5 - 10^9$ cm^{-3}, high-volume sampling is needed in order to concentrate R as spin adducts in the amount sufficient for EPR recording. So a spin trap should be stable in the presence of oxidizers, which are abundant in air (O$_2$, O$_3$, NO$_2$, etc.). When tested in natural atmospheric conditions, compounds **4**, **8**, and **17** were stable and produced no background signals. The formation of spin adducts in the spin trapping of R from polluted air (vehicle exhaust) was observed.

Compounds **3** and **5** cannot be recommended for use under atmospheric conditions, since **3** produced only a strong triplet while **5** was easily blown off the filter during sampling.

Thus, nitrones **4, 5, 8**, and **17** can be used for spin trapping

of OH from the gas phase, and **3−5** and **17** can also trap organic SFRs. Nitrones **4, 8**, and **17** can be recommended as spin traps under atmospheric conditions.

Conclusions.

1. Acyclic α-phenylnitrones **1−4** are spin traps for CH$_2$OH radicals. Only **4** traps the OH radical. EPR parameters of spin adducts are close to those of known acyclic spin adducts, but the presence of functional groups (keto or oxime) has changed the trapping properties (e.g., selectivity to different radicals).

2. Cyclic dinitrones **5−15** are efficient spin traps for both OH and hydroxyalkyl radicals, except **11** which traps only OH. These dinitrones form adducts with only one radical center. The nitrone structure, particularly in the presence of substituents, causes changes in a_H of adducts with the same R in the range 0.92−2.00 mT. Large values of a_H help to distinguish among spin adducts of different radicals. Conjugation of nitrone groups has no influence on the spin-trapping properties.

3. Imidazoline nitrones **16** and **17** are spin traps for a series of R. It is found for the first time that EPR parameters of the spin adducts of **17** are strongly dependent on pH, which is caused by the protonation of the amino nitrogen of **17**.

4. Nitrones **7** and **17** are able to trap HO$_2$ radical. The lifetimes of the spin adducts (3 and 8 min, respectively) are longer than those for the known spin traps.

5. The nitrones **3−5, 8**, and **17** are efficient spin traps for gas phase R, including organic ones. Among these nitrones, **4, 8**, and **17** can be recommended as spin traps for detecting R in the atmosphere.

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Spin Traps

J. Phys. Chem., Vol. 100, No. 44, 1996 **17527**

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