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A Mild Dehydrazination Reaction of Arylhydrazines Using Nitric Oxide in the Presence of Oxygen

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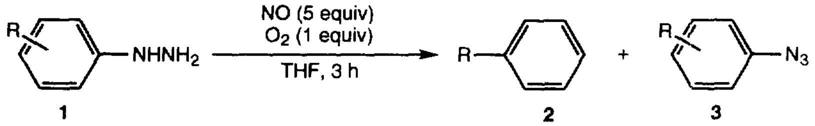
Abstract: A new dehydrazination reaction of arylhydrazines using nitric oxide and oxygen as a mild nitrosating agent is described. Taking advantage of non-aqueous and non-acidic medium appears to cause this novel selectivity as a counterpart of the azide synthesis by the conventional methods. The generality and reaction mechanism were also investigated. © 1997 Elsevier Science Ltd.

Although nitric oxide (NO) is a simple radical molecule, it has diverse physiological roles such as muscle relaxation, neurotransmission, regulation of immune functions, and so on.[1] Because of the well-recognized importance of NO, extensive research has been carried out from the viewpoints of biochemistry and physiology.

Recently, much attention has been paid to the reactivities of NO in the field of chemistry, and papers concerning the chemistry of NO have been gradually increasing in a last few years. The studies concerning NO seem to be divided into three types: employment of NO as a mild nitrosation or nitration reagent to exploit new organic reactions,[2] development of the detection method of NO in the biological system using organic reactions,[3] and reactions of NO with biologically important molecules.[4] We have been studying the reactivity of NO toward nitrogen-containing compounds, and it was revealed that NO shows various reactivities dependent on the structures of substrates and the amounts of O_2 supplied to reaction systems. That is, Hantzsch dihydropyridines were found to be readily aromatized in the action of NO as an oxidizing agent,[5] and aromatic primary amines were revealed to react with NO in the presence of a catalytic amount of O_2 in THF solution to bring about deamination reaction.[6] Moreover, it was found that amides reacted with NO to afford *N*-nitrosoamides and that this reaction was accelerated by the addition of O_2.[7] These results suggest us that compounds which contain an N-H bond might react with NO in various ways under the influence of O_2. Thus, other substrates containing an N-H bond were investigated, and arylhydrazines are found to react with NO in the presence of O_2 to afford benzene derivatives.[8] This result prompted us to reveal its generality and detailed reaction mechanism. This paper describes these results.

There are some reports which claimed the conversion of phenylhydrazine to phenylazide by *N*-nitrosation reaction, and *N*-nitrosation reagents used for the reaction involved nitrous acid,[9] clay-supported ferric nitrate,[10] dinitrogen tetroxide,[11] and nitrosonium tetrafluoroborate.[12] The dehydrazination reaction, however, has never been reported under such *N*-nitrosation conditions.[13] When arylhydrazines **1** were subjected to the reaction with NO in THF in the presence of oxygen, benzene derivatives **2** were obtained accompanied by small amounts of arylazides **3** (Scheme 1 and Table 1).



Scheme 1

At first, the substituent effects on the yield and selectivity were examined. As a standard procedure, 5 equiv of NO and 1 equiv of O_2 were employed in THF at room temperature. As shown in Table 1, the more highly electron-donating substituent was introduced, the higher selectivity toward the formation of the dehydrazinated products was observed in the case of *p*-substituted derivatives (entries 2 - 5), while *o*- and *m*-substituted derivatives showed reverse selectivity for the products (entries 6 - 9 and entries 10 - 13). Comparison among isomeric compounds revealed that the selectivity was higher for the *p*-substituted derivatives than the *o*- and *m*-substituted derivatives in the cases of Cl- (entries 3, 7, and 11), Me- (entries 4, 8, and 12), and MeO- (entries 5, 9, and 13) derivatives. On the contrary, it was found that *p*-nitrophenylhydrazine was less selective than *o*- and *m*-nitro derivatives (entries 2, 6, and 10). 2,4-Dinitrophenylhydrazine, which possesses strong electron-withdrawing groups so that its α-nitrogen is not likely to have reactivity toward electrophile,[9] had a tendency to form the corresponding azide as a major product (entry 14). Interpretation of these results will be considered later with the reaction mechanism.

Table 1 Reaction of Arylhydrazines **1** with NO in the Presence of O_2

Entry	Substrate	R	Yield of **2** (%)	Yield of **3** (%)	Ratio (**2**/**3**)
1	**1a**	H	76	20	3.80
2	**1b**	*p*-NO_2	61	25	2.44
3	**1c**	*p*-Cl	77	13	5.92
4	**1d**	*p*-Me	82	10	8.20
5	**1e**	*p*-MeO	72	8	9.00
6	**1f**	*m*-NO_2	55	14	3.93
7	**1g**	*m*-Cl	62	17	3.65
8	**1h**	*m*-Me	60	19	3.16
9	**1i**	*m*-MeO	43	15	2.87
10	**1j**	*o*-NO_2	64	17	3.76
11	**1k**	*o*-Cl	45	17	2.65
12	**1l**	*o*-Me	49	37	1.32
13	**1m**	*o*-MeO	29	59	0.49
14	**1n**	2,4-diNO_2	30	61	0.49

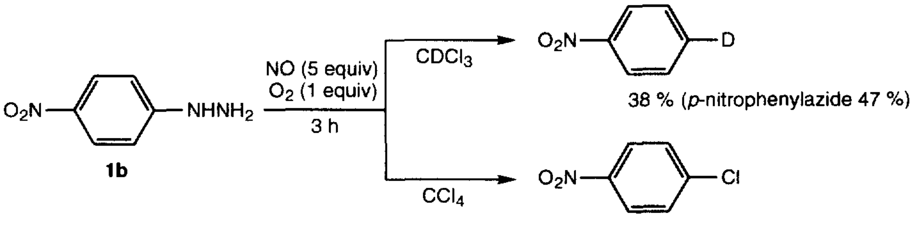
The reaction was carried out in 5 equiv of NO and 1 equiv of O_2.

Next, solvent effects were investigated using **1a** as a substrate, and considerable solvent effects were observed as shown in Table 2. THF was the best solvent for the formation of **2** under the standard conditions, and other ethereal solvents afforded moderate yields. CH_3CN and CH_2Cl_2 were not suitable for this reaction. These results are in accord with the previous data of the deamination reaction[14] whose reaction pathway involves the intermediary formation of aryl radicals.[6] Thus, it was suggested that an aryl radical was formed as a precursor of **2**, being same as the case of the deamination reaction. When *p*-nitrophenylhydrazine (**1b**) was treated with NO and O_2 using $CDCl_3$ or CCl_4 as a solvent, the *p*-deuteriated or *p*-chlorinated product was produced respectively, without the hydrogenated one (Scheme 2). These results also suggested the formation of an aryl radical intermediate which abstracts hydrogen from the solvent.

Table 2 Solvent Effect on the Reaction of Phenylhydrazine **1a** with NO and O_2

Solvent	Yield of **2a** (%)	Yield of **3a** (%)	Ratio (**2a**/**3a**)
THF	76	20	3.80
DME	53	21	2.52
$CHCl_3$	52	40	1.30
MeCN	12	33	0.36
1,4-dioxane	47	23	2.04
CH_2Cl_2	16	48	0.33

The reaction was carried out using **1a** as a substrate with 5 equiv of NO and 1 equiv of O_2 for 3 h.



Scheme 2

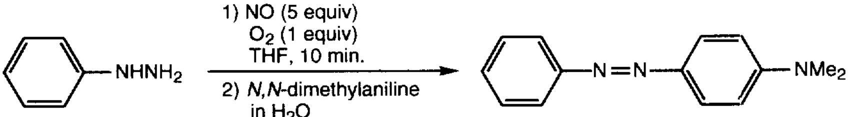
The reaction yields of **2a** and **3a** using various amounts of NO and O_2 were investigated to elucidate the stoichiometry of the reaction. As shown in entries 1 - 4 in Table 3, 0.5 equiv of O_2 was necessary for the completion of the reaction. The results indicated that a true reactive species is not NO but other higher nitrogen oxides such as N_2O_3, and that in this reaction system oxygen does not act in a catalytic fasion, which is different from the previously reported deamination of the aromatic primary amines.[6] A further increase of the O_2 amount gradually reduced the yield of **2** (entries 5 and 6). These facts suggest highly oxygenated nitrogen oxide, probably NO_2, has low selectivity in the reaction. The use of NO_2 itself showed low selectivity as expected (entry 7), though the yield of **2** was lower than those of entries 5 and 6. These findings indicate that the formation of NO_2 is incomplete in the mixture of NO and $1/2O_2$. Upon these results, the amount of NO was varied in the presence of 0.5 equiv of O_2 (entries 8 - 11). The completion of the reaction was achieved when 3 equiv of NO was applied (entry 10), but the yield of **2** was higher in the case that more than 4 equiv of NO was used (entries 11 and 3). The experiment using a *p*-nitro derivative **1b** revealed that this substrate is less reactive than unsubstituted one especially under the conditions of low amounts of NO and O_2, though the selectivity seems to be equal (Table 3).

Table 3 Effect of the Amount of NO and O_2 on the Reaction of Phenylhydrazine **1a** with NO

Entry	NO (equiv)	O_2 (equiv)	Time (h)	Yield of **2** (%)	Yield of **3** (%)	Ratio (**2**/**3**)	Recovery (%)
1	5	0	3	0 (0)	0 (0)	— (—)	67 (96)
2	5	0.2	3	20 (5)	12 (13)	1.67 (0.38)	20 (52)
3	5	0.5	3	75 (59)	19 (19)	3.95 (3.11)	0 (0)
4	5	1	3	76 (61)	20 (25)	3.80 (2.44)	0 (0)
5	5	2	3	52 (54)	25 (27)	2.08 (2.00)	0 (0)
6	5	3	3	55 (50)	24 (31)	2.29 (1.61)	0 (0)
7	NO_2 (5 equiv)		3	35 (51)	25 (31)	1.40 (1.77)	0 (0)
8	1	0.5	24	24 (trace)	12 (10)	2.00 (—)	20 (43)
9	2	0.5	24	31 (43)	37 (18)	0.82 (2.39)	0 (0)
10	3	0.5	7	74 (58)	25 (23)	2.96 (2.52)	0 (0)
11	4	0.5	7	79 (60)	20 (18)	3.95 (3.33)	0 (0)

Yields and ratio shown in the parentheses are the data using **1b** as a substrate.

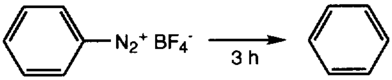
The products or intermediates obtained from *N*-nitrosation of arylhydrazines are reported to involve corresponding α-nitroso, β-nitroso, azide derivatives, and diazonium salts.[9] Thus, these compounds other than unisolable β-nitroso derivative were subjected to the reaction with NO and O_2 in THF to examine their reactivities. It was confirmed that arylazides were entirely stable under the standard reaction conditions, thus the azide was proved not to be a precursor of **2**. Diazonium salt is known to be produced by further nitrosation of α- or β-nitroso derivatives followed by elimination of N_2O.[9] In fact, when phenylhydrazine (**1a**) was allowed to react under the standard conditions and the reaction was stopped in 10 minutes, the corresponding diazonium salt was detected in 20% yield as a corresponding azo-dye (Scheme 3). Thus, the reactivity of benzenediazonium tetrafluoroborate, prepared by a reported method,[15] was investigated. It was found that benzenediazonium salt was partly denitrogenated to afford benzene when suspended in THF (20% yield), but the addition of NO (5 equiv) and O_2 (1 equiv) to this system did not influence the reaction yield (Scheme 4).[16] These results show that the solvent itself is supposed to function as a reductant of diazonium salt,[17] although the yields are considerably low.



1a

20 %

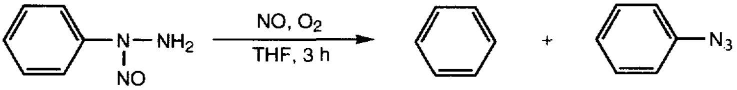
Scheme 3



THF under Ar : Yield 20 %
THF in the presence of NO (5 equiv) and O_2 (1 equiv) : Yield 20 %

Scheme 4

Readily isolable α-nitrosophenylhydrazine (**4**) is known to rearrange and be dehydrated to yield phenylazide under acid catalyzed conditions.[18] Thus, compound **4** was synthesized according to a reported method[18] and its reactivity was investigated (Scheme 5 and Table 4). Compound **4** was found to be stable in THF solution under Ar atmosphere (entry 1). In the presence of a trace amount of TsOH, however, **4** was readily converted to phenylazide (entry 2), as is in accord with a literature precedent.[18] When **4** was subjected to the reaction under the standard condition (5 equiv of NO and 1 equiv of O_2), degradated product **2a** was formed in a moderate yield, accompanied by a corresponding diazonium salt in 16% yield (entry 3). The applyment of the reduced amount of reagents at the same NO/O_2 ratio brought about the considerably efficient conversion of **4** to benzene (entry 4), thus compound **4** was shown to be one of the most plausible precursors of **2**. When equimolar amount of NO was used (entry 4), a corresponding amount of N_2 was evolved from the reaction mixture, which was confirmed by GLC (see Experimental). The decreased amount of NO caused the lowering of the yield, which suggested the stoichiometric amount of NO was necessary for the formarion of **2** (entries 5 and 6). Even in the presence (or the absence) of a catalytic amount of oxygen, the reaction proceeded smoothly (entries 7 and 8), thus the role of oxygen in this step remains unclear.[19]



4 **2a** **3a**

Scheme 5

Table 4 Reaction of α-Nitrosophenylhydrazine **5** with NO and O_2

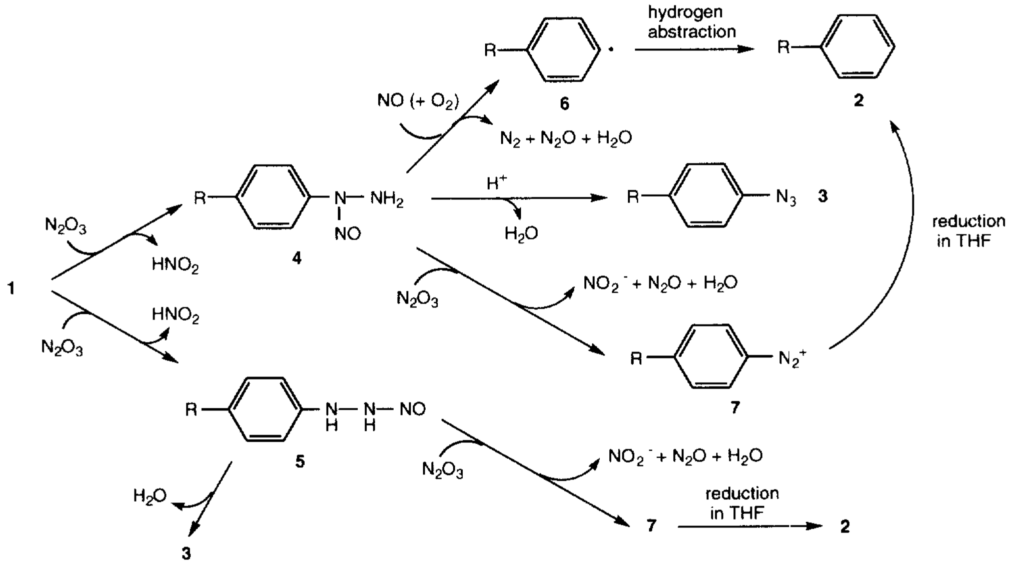
Entry	NO (equiv)	O_2 (equiv)	Yield of **2a** (%)	Yield of **3a** (%)
1	0	0	0	0
2 a)	0	0	16	72
3	5	1	53 b)	4 b)
4	1	0.2	85	6
5	0.5	0.1	28	3
6	0.1	0.02	6	trace
7	1	0.0002[19]	90	8
8	1	0[19]	27	1

a) In the presence of a catalytic amount of TsOH.
b) The corresponding diazonium salt was also detected in 16% yield as an azo-dye.

Based on these results, the reaction mechanism is supposed as shown in Scheme 6. The initial step might be the nitrosation of α- or β-nitrogen by N_2O_3, which was formed by the reaction of NO with O_2. α-Nitrosation of arylhydrazines afforded **4**, and it was transformed to three different compounds depending upon the reaction conditions. In the presence of an equimolar amount of NO, compound **4** was converted to an aryl radical **6**, which abstract hydrogen from the solvent to afford product **2**. When acidic proton exists, which should be formed *via* the first nitrosation step, **4** was rearranged to arylazide **3** after dehydration. As shown in Table 3, the increase of the amount of oxygen slightly increased the formation of

3. This result is rationally reasoned by the fact that nitrite is less acidic than nitrate which is more formed in the presence of much oxygen. When N_2O_3 (or other nitrosation reagents) exists in excess, second nitrosation toward **4** might occur to give a diazonium salt **7** through the release of N_2O and OH^-. Thus, the dehydrazination newly found in our reaction system was supposed to be caused by the suppression of the use of excess amount of nitrosation reagent and the weaker acidic medium than those of the conventional methods. β-Nitroso derivative is supposed to be converted to the diazonium salt if further nitrosation occurs, or be dehydrated to afford azide. These processes have already suggested in a previous paper.[9] Diazonium salt **7** was partly reduced in THF to form **2** probably through the aryl radical, but this conversion was not effective in the case of phenyldiazonium tetrafluoroborate. In addition, aryldiazonium salts which have electron-donating substituent at *m*-position was known to be labile and decomposed readily,[6] thus the results shown in entries 8 and 9 in Table 1 suggest that the pathway through the diazonium salts was less important for the formation of **2**.

When there is an electron-withdrawing group on phenyl group, α-nitrosation becomes less advantageous than β-nitrosation, thus intermediate **5** is thought to be dominant to afford **3** and **7**. This might be the reason why electron-deficient arylhydrazines have a tendency to give more arylazides than electron rich ones (Table 1, entries 2-5). It was supposed, however, that an electron-withdrawing substituent on the diazonium ion **7** facilitates the reduction by THF to give **2**. Therefore, in the cases of electron-deficient arylhydrazines, the pathway from **7** to **2** might function as a major process.



Scheme 6

When *o*-substituted arylhydrazines were substrates, the steric factor might hinder the α-nitrosation even in the cases of electron rich hydrazines. Thus the efficient pathway for the formation of **2** (**4** → **6** → **2**) did not function, and the reduction of **7** was disadvantageous in these substrates to give rise to the dominant formation of azides (Table 1, entries 13-14).

In this paper, we described a new dehydrazination reaction using NO and O_2 in THF solvent. It was revealed that NO in the presence of small amounts of O_2 acts as a mild nitrosating agent in non-acidic medium. The reaction system is thought to be of synthetic use because the reaction and the work-up procedure are quite operationally simple. Application of this reaction system to the other nitrogen-containing compounds and elucidation of the general aspects on the chemical reactivities of NO are now in progress.

EXPERIMENTAL

All melting points were taken on Büchi 535 micro melting point apparatus and are uncorrected. The nuclear magnetic resonance spectra (NMR) were measured with JEOL GX400 and LA500 spectrometers using tetramethylsilane as an internal standard. HPLC analysis was performed using JASCO TRI ROTAR-V pump and JASCO UVIDEC-100-V UV spectrophotometer.

Reagents and Authentic Samples All arylhydrazines were of analytical grade and were used as received. Some of them were purchased as salts with HCl and free hydrazine was obtained by the procedure that its aqueous solution was treated with solid K_2CO_3 followed by CH_2Cl_2 extraction. It was necessary for free hydrazines obtained by the above procedure to be used for the reaction as soon as possible because of their instabilities. Solvents used for the reaction were needed to be freshly distilled to obtain reproducible results. Nitric oxide gas (99.9%) was purchased from Takachiho Chemical Company Ltd, and was passed through 10M NaOH solution to remove NOx impurities and then through a column of solid $CaCl_2$ and KOH for dryness. Phenylazide was prepared using a reported method[20] and substituted derivatives were also synthesized in a similar manner (All of them are reported compounds[21]). All the compounds obtained from degradation of arylhydrazines were commercially available.

General Procedure of the Reaction of Arylhydrazines with NO and O_2 Arylhydrazine (0.2 mmol) was placed in a two necked flask (80 ml volume) and dissolved in freshly distilled THF (10 ml), then this solution was bubbled with Ar gas for 20 min through a gas inlet tube. The atmosphere in the flask was completely replaced with Ar gas and the flask was sealed with a stopcock and a septum rubber. Then O_2 (4.48 ml) was added with a micro syringe and NO gas (22.4 ml) measured using Hamilton gas-tight syringe was added to the reaction vessel. The reaction mixture was allowed to stand for 3 h at room temperature. Then Ar gas was bubbled to remove excess NO and the product was analyzed with ^{1}H-NMR or HPLC. The identifications of the products were performed comparing with physical and spectral data of authentic samples. The product yields were determined by ^{1}H-NMR using mesitylene as an internal standard or by HPLC using biphenyl or naphthalene as an internal standard.

Trapping of the Intermediary Diazonium Salt by Diazo Coupling Phenylhydrazine (0.2 mmol) was allowed to react under the same conditions mentioned above for 10 min. After the removal of excess NO, THF was evaporated off at room temperature and the residue was dissolved in 25% aqueous AcONa solution (5 ml), then *N,N*-dimethylaniline (0.5 mmol) was added. The mixture was stirred at room temperature for 1 h, and made basic with 1N NaOH. After the extraction with CH_2Cl_2, the organic layer was dried over $MgSO_4$, and evaporated off to leave a residue, which was purified with silica gel chromatography. The yellowish crystal (9 mg) thus obtained was identical with the authentic sample synthesized in a preceding paper.[6b] Yield 20%.

Reduction of Benzenediazonium Tetrafluoroborate in THF Benzenediazonium tetrafluoroborate was prepared from aniline and nitrosonium tetrafluoroborate according to a reported method.[15] Benzenediazonium tetrafluoroborate (0.2 mmol) was suspended in THF and allowed to stand at room temperature for 3 h under Ar atmosphere. The yield of benzene (20%) was estimated with HPLC analysis. The experiment in the presence of NO (22.4 ml) and O_2 (4.48 ml) gave the same result.

Reaction of α-Nitrosophenylhydrazine with NO and O_2 α-Nitrosophenylhydrazine was prepared as follows, since a detailed procedure was not described in a preceding literature.[18] That is, the solution of phenylhydrazine hydrochloride 1.45 g (10 mmol) and AcONa 1.64 g (10 mmol) in H_2O (30 ml) was cooled on ice bath and $NaNO_2$ 690 mg (10 mmol) was added to this mixture. The reaction temperature was elevated to room temperature and the mixture was allowed to react for additional 1 h. Resultant mixture was extracted with CH_2Cl_2 and the organic layer was washed with H_2O several times to remove remaining starting material, then dried over $MgSO_4$ and evaporated off. An oily residue thus obtained was suspended in hexane and cooled to afford precipitate, which was collected by filtration and washed with hexane. Colorless powder 166 mg (12%). Mp 49 - 50°C (lit.[18] mp 50°C). α-Nitrosophenylhydrazine thus obtained was immediately allowed to react under several conditions according to the general procedure. The yields of benzene and phenylazide were determined with HPLC. The detection of diazonium salt was performed using diazo coupling method mentioned above.

Determination of the Amount of N_2 Generated in the Reaction of 4 with NO α-Nitrosophenylhydrazine (**4**) (27 mg, 0.2 mmol) was placed in a two necked flask (35 ml volume) and reacted with NO (1 equiv) anJ O_2 (0,2 equiv) according to the general procedure for 3 h. After the completion of the reaction, the gas phase in the reaction vessel was quantitatively analyzed with a gas chromatography (GC). GC analysis was performed using a Shimadzu GC-14BPTF equipped with TCD and packed column Molecular Sieve 5A 60/80 (3 m X 3Φ) maintained at 100°C.

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14. In the reaction, the solvent acted as a hydrogen donor to a phenyl radical. In the case of using $CHCl_3$ as a solvent, the yield of **2** was lower than that expected from ref. 6, although the good conversion yield was observed. Probably, a trace amount of acidic impurities of $CHCl_3$ might affect the product distribution.

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19. In our reaction, 0.0002 equiv of NO means the addition of 1 μl of NO to the reaction vessel of ca. 80 ml. We did try to exclude oxygen completely in the case of entry 8 in Table 4, but there is possibility that a trace amount of oxygen (probably <0.3 μl) was contaminated in the vessel.

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