oxy]-4-[3-[(tetrahydro-2*H*-pyran-2-yl)oxy]-1-octenyl]-2-methoxy-2*H*-cyclopenta[*b*]furan-2-ol, 69928-04-7; hexahydro-6-fluoro-5-[(tetrahydro-2*H*-pyran-2-yl)oxy]-4-(3-hydroxy-1-octenyl)-2*H*-cyclopenta[*b*]furan-2-one, 69928-05-8; sodium 5-(triphenylphosphoranylidene)pentanoate, 41723-91-5; i, 69928-06-9.

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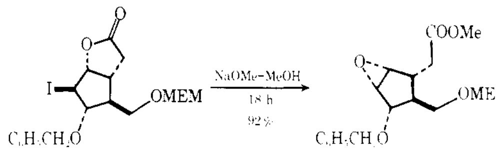

i 13 (2)

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Activation of Reducing Agents. Sodium Hydride Containing Complex Reducing Agents. 10.[1] NaH–RONa–Co(OAc)$_2$–CO, a New Reagent for the Carbonylation of Aryl Halides at Atmospheric Pressure

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The preparation of CoCRA (NaH–RONa–Co(OAc)$_2$) under carbon monoxide at atmospheric pressure led to cobalt carbonyl species of unprecedented reactivity. These new reagents, designated as CoCRACO, were found to be very efficient for the carbonylation of aryl halides at *atmospheric pressure*. Mixtures of aromatic acids and esters were obtained in good yields. Carbonylation of aryl halides in the presence of amines led to benzamides. Furthermore, it was demonstrated that all these reactions were catalytic with respect to cobalt.

It is well known that the preparation of cobalt carbonyl species from cobalt salts in aprotic media requires rather drastic conditions.[2] To our knowledge, only the use of iron-manganese alloy allows the preparation of active carbonyl species from cobalt salts at atmospheric pressure.[3]

Current literature also indicates that extreme conditions of reaction temperature and pressure are required for the carbonylation of aryl halides by cobalt carbonyl species.[4] The carbonylation of such halides is generally best achieved by nickel carbonyl species. Note that the presence of bases is often reported as favoring this kind of reaction; it is generally assumed that anionic carbonyl species react more easily with aryl halides than do neutral species.[5,6]

If we now consider the preparation and properties of complex reducing agents "NaH–RONa–MX$_n$" (abbreviated MCRA),[7] it could be thought that a preliminary reduction of metallic salts by NaH–RONa occurs and that, during the formation of MCRA, low oxidation state metal species and bases are simultaneously present. Thus, if some efficient ligands (like phosphines, dienes, or carbon monoxide) were simultaneously present, a stabilized low oxidation state complex should result instead of a reducing species.[8] Moreover, with carbon monoxide as ligand, anionic species should be reasonably expected.[9]

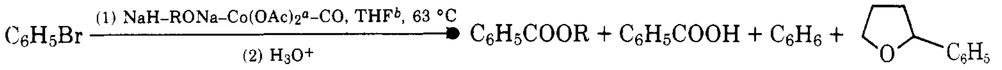
Some preliminary results verified these hypotheses.[10] Indeed, it was shown that preparation of CoCRA (NaH-*t*AmONa-Co(OAc)$_2$) under a slow stream of carbon monoxide led to cobalt carbonyl species (abbreviated here as CoCRACO for convenience) which were able to carbonylate aryl bromides at atmospheric pressure. However, subsequent studies showed that these reactions were of poor reproducibility. As a matter of fact, without apparent reason, reduction sometimes exceeded carbonylation. We therefore reinvestigated these reactions, and we can now report a highly reproducible method for the carbonylation of aryl halides at atmospheric pressure.

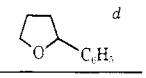
Results and Discussion

The Carbonylating Medium: NaH–RONa–Co(OAc)$_2$–CO (CoCRACO). In our previous work,[10] the cobalt carbonyl species were prepared by adding Co(OAc)$_2$, at 25 °C, to a suspension of NaH-*t*-AmONa in THF under a slow stream of carbon monoxide. The reaction medium was then warmed to 63 °C and stirred for 4 h before adding the aryl halide. Taking into account the poor reproducibility of the carbonylation reaction vs. reduction with the reagents thus obtained, a systematic study of reaction conditions was undertaken using bromobenzene as a test substrate.

This study led us to the following general procedure (more details are given in the Experimental Section): At room tem-

Table I. Carbonylation of C_6H_5Br by CoCRACO; Variation of the Alkoxide



R (from RONa)	reaction time, h	% recovered[c] C_6H_5Br	% reduction[c] to C_6H_6	overall carbonylation[d] yield, %	ester/acid ratio	 [d]
methyl	20	100				
ethyl	3		55–60	20–25	55/45	10
ethyl[e]	40	40	0–5	50–55	65/35	traces
neopentyl	20	traces	5–10	80–85	85/15	traces
1-octyl	40	60	0–5	30–35	25/75	10
cyclohexyl	42	5	10–15	65–70	45/55	10
2-octyl	40	5	15–20	80–85	85/15	traces
tert-amyl	24	5	10–15	65–70	75/25	5
tert-butyl	42	10	10–15	70–75	80/20	traces
allyl	95	20	10–15	55–60	*f*	traces[g]

[a] NaH/RONa/Co(OAc)$_2$/C_6H_5Br = 40/20/10/20 mM. [b] 50 mL. [c] Determined by GLC analysis with internal standards. [d] Isolated yields based upon starting aryl halide (20 mM). [e] Experiment performed at 40 °C. [f] No ester was formed. [g] Formation of 5% benzil and 2–5% biphenyl was registered.

Table II. Carbonylation of Aryl Halides by CoCRACO

$$\mathrm{ArX} \xrightarrow[\text{(2) H}_3\text{O}^+]{\text{(a) NaH-}\textit{neo}\text{-PeONa-Co(OAc)}_2{}^a\text{-CO, THF,}^b\ 63\ ^\circ\text{C}} \mathrm{ArCOOCH_2C(Me)_3 + ArCOOH + ArH}^c$$

ArX	reaction time, h	% recovered[d] ArX	% reduction[d] to ArH	overall carbonylation yield, %[e]	ester/acid ratio
C_6H_5Cl	52	60	traces	35–40	20/80
C_6H_5Br	10	5	15–20	80–85	45/55
C_6H_5I	1		15–20	70–75	10/90
o-MeC_6H_4Br	25	10	0–5	80–85	45/55
m-MeC_6H_4Br	20	10	traces	85–90	45/55
p-MeC_6H_4Br	20	5	traces	90–95	60/40
o-$MeOC_6H_4Br$	15		traces	95–100	60/40
m-$MeOC_6H_4Br$	15	10	traces	90–95	55/45
p-$MeOC_6H_4Br$	15	traces	traces	95–100	55/45
p-FC_6H_4Br	20	10	traces	85–90	55/45
p-$MeC(O)C_6H_4Br$	25	10	5–10	80–85	55/45
p-$Me_2NC_6H_4Br$	15	10	45–50	35–40	10/90

[a] NaH/*neo*-PeONa/Co(OAc)$_2$/ArX = 40/20/10/10 mM. [b] 50 mL. [c] In all cases, side reactions were observed leading to traces of unidentified byproducts which are believed to be 2-aryltetrahydrofurans. [d] Determined by GLC analysis with internal standards. [e] Isolated yields based upon starting aryl halide (10 mM).

perature, the cobalt salt was added to a stirred mixture of NaH-*t*-AmONa in THF under a slow stream of carbon monoxide. After the mixture was stirred for 2 h, bromobenzene was added and the temperature was raised to 63 °C (the carbon monoxide stream was continued). Under these conditions, carbonylation of bromobenzene *reproducibility* afforded mixtures of benzoic acid and *tert*-amyl benzoate in good yields.

The activating alkoxide plays an important role on the properties of MCRA.[11] Thus we studied this variable in the carbonylation of C_6H_5Br using different alkoxides. As may be seen in Table I, the activity order observed has some analogy with that for complex bases.[7] Tertiary, secondary, and neopentyl alcohols were very efficient for the preparation of CoCRACO while allyl alcohol, which is a good activating agent for sodamide,[7] was less active. Thus, neopentyl alcohol was selected for further studies.[12]

The influence of the solvent on the carbonylation reaction was briefly examined. Among the solvents studied (THF, DME, DMF, anisole, benzene), THF led to the best results.

With THF as solvent, small amounts of 2-phenyltetrahydrofuran and biphenyl were frequently observed, indicating the formation of phenyl radicals. Small amounts of benzil were also formed, probably originating from benzoyl cobalt species.[13] Thus, although the actual nature of CoCRACO is still unknown, we now have strong evidence for the formation of aryl and aroyl cobalt carbonyl species.

The formation of benzoic acid was more intriguing. Control experiments showed that neopentyl benzoate was partially saponified by either NaH-*neo*-PeONa (*neo*-Pe = neopentyl) or CoCRA or CoCRACO to yield benzoic acid and neopentyl alcohol. These reactions may result from sodium hydroxide in the NaH or traces of water in the system. However, as may be seen from Table II, carbonylation of iodobenzene led to benzoic acid in up to 55–60% yield. This result cannot be explained only by the saponification of benzoic acid esters and suggests that part of the acid was formed by hydrolysis of a benzoylcobalt species during the workup. Thus, both ester saponification and benzoylcobalt hydrolysis may account for the formation of benzoic acid.

Cobalt carbonyl species in CoCRACO exhibit an unprecedented reactivity for cobalt systems and none of the common carbonyl species may account for the observed reactions. Indeed, literature data indicate that $Co_2(CO)_8$ does not easily react with aryl halides;[13] on the other hand, $HCo(CO)_4$ seems too acid a species to survive in the reaction medium during the preparation of the reagents.[14] Finally, as with most metal carbonyl anions,[15] $Co(CO)_4^-$ appears as a poorly nucleophilic

Table III. Catalytic Carbonylations of Aryl Halides by CoCRACO

$$\mathrm{ArX} \xrightarrow[\text{(2) } \mathrm{H_3O^+}]{\text{(1) NaH–}\textit{neo}\text{-PeONa–Co(OAc)}_2{}^{a}\text{–CO, THF,}^{b}\text{ 63 °C}} \mathrm{ArCOOCH_2C(Me)_3 + ArCOOH + ArH}^{c}$$

					overall carbonylation yield, %[f]	
ArX	reaction time, h	% recovered ArX[d]	% reduction to ArH[d]	ester/acid[e]	with respect to ArX	with respect to cobalt
C_6H_5Br	45	15	0–5	70/30	80–85	800–850
p-MeC_6H_4Br	45	10	5–10	55/45	70–75	700–750
p-$MeOC_6H_4Br$	45	10	20–25	45/55	55–60	550–600
p-FC_6H_4Br	50	20	10–15	55/45	65–70	650–700
p-$MeC(O)C_6H_4Br$	60	15	10–15	55/45	65–70[g]	650–700

[a] NaH/*neo*-PeONa/Co(OAc)$_2$/ArX = 200/100/10/100 mM. [b] 50 mL. [c] In all cases, side reactions leading to traces of unidentified byproducts were observed. [d] Determined by GLC analysis with internal standards. [e] Molar ratio. [f] Isolated yields. [g] Small amounts of *p-tert*-amyloxyneopentyl benzoate were isolated.

Table IV. Carbonylation of C_6H_5Br by CoCRACO in the Presence of Amines

$$\mathrm{C_6H_5Br} \xrightarrow[\text{(2) } \mathrm{H_3O^+}]{\text{(1) NaH/}t\text{-AmONa/amine/Co(OAc)}_2{,}^{a}\text{ CO, THF,}^{b}\text{ 63 °C}} \mathrm{C_6H_5C(O)N<} + \mathrm{C_6H_5COO\text{-}}t\text{-}\mathrm{Am} + \mathrm{C_6H_5COOH}$$

amine	reaction time, h	% recovered[c] C_6H_5Br	% reduction[c] to C_6H_6	amide[d] yield, %	ester[d] yield, %	acid[d] yield, %	overall[d] carbonylation yield, %
n-$C_4H_9NH_2$[e]	48	25	10–15	30–35	0–5	10–15	50–55
n-$C_8H_{17}NH_2$[e]	40	20	10–15	40–45	5–10	10–15	60–65
c-$C_6H_{11}NH_2$	20	5	5–10	70–75	traces	5–10	80–85
Et_2NH	45	5	10–15	40–45	20–25	5–10	65–70
$(i$-$Pr)_2NH$	25	5	5–10	30–35	30–35	15–20	80–85
$C_5H_{11}N$	25	5	10–15	45–50	5–10	15–20	75–80

[a] NaH/*t*-AmONa/amine/Co(OAc)$_2$/C_6H_5Br = 40/20/40/10/20 mM. [b] 50 mL. [c] Determined by GLC analysis with internal standards. [d] Isolated yields based upon the starting C_6H_5Br (20 mM). [e] With these amines, formamides were obtained. For *n*-BuNH$_2$, HCONHBu: 400 mg, i.e., ~4 mM, and for *n*-$C_8H_{17}NH_2$, HCONH-*n*-C_8H_{17}: 470 mg, i.e., ~3 mM.

species in aromatic substitution reactions. A difficult problem thus remains to be solved in the future, i.e., the determination of the actual nature of active species which must be very reactive.

Carbonylation of Aryl Halides. The above results were extended to chloro- and iodobenzene and subsequently to substituted aryl bromides. Except for *p*-(dimethylamino)bromobenzene, all substituted aryl bromides were carbonylated in very good yields (Table II). In most cases, reduction to benzene derivatives was not very substantial. Furthermore, carbonylation of chlorobenzene in such mild conditions is unprecedented.[16]

Carbonylation of *p*-dibromobenzene yielded reproducibly 60–65% terephthalic acid derivatives, 5–10% *p*-bromobenzoic acid, and 10–15% benzoic acid. On the contrary, *p*-chlorobenzoic acid ethyl ester led to only 10–15% benzoic acid and 85–90% *p*-chlorobenzoic acid.[17]

Catalytic Carbonylations. Carbonylation of aryl bromides was performed by using cobalt salt in catalytic amounts. Results reported in Table III clearly indicate that CoCRACO may function as a catalytic reagent. These results indicate a quite rapid regeneration of CoCRACO from NaH–RONa–CO and the cobalt species formed during the carbonylation.

Carbonylation of C_6H_5Br in the Presence of Amines. The alkoxide part of CoCRACO plays the role of nucleophile to lead to benzoic acid esters. So, in the simultaneous presence of other nucleophiles (such as amines), it should be possible to obtain benzoyl derivatives (such as benzamides). Indeed, under slightly different conditions (in particular using *t*-AmONa instead of *neo*-PeONa), amines efficiently compete with *t*-AmONa to yield benzamides in rather good yields (Table IV). In some cases, the formation of formamides was observed, which probably arose from direct carbonylation of amines.[18]

Scheme I

$$\mathrm{C_6H_5Br} \xrightarrow[\text{(2) } \mathrm{H_3O^+}]{\text{(1) NaH–C}_5\text{H}_{11}\text{N–Co(OAc)}_2{,}^{a}\text{ CO, THF, 63 °C, 30 h}}$$

$$\underset{40\%}{\mathrm{C_6H_5C(O)NC_5H_{10}}} + \underset{25\%}{\mathrm{C_6H_5COOH}} + \underset{5\%}{\mathrm{C_6H_5CHO}} + \underset{20\%}{\mathrm{C_6H_6}}$$

[a] NaH/$C_5H_{11}N$/Co(OAc)$_2$/C_6H_5Br = 60/40/10/20 mM. 90% conversion.

Control experiments showed that, in simulated reaction conditions, formation of benzamides from benzoic acid esters and amines occurred in only 5–10% yield. Note that *N*-benzoylpiperidine reacted with CoCRACO to yield (60% conversion in 24 h) benzoic acid (25–30%), benzaldehyde (25–30%), benzoic acid *tert*-amyl ester (traces), and 2-phenyltetrahydrofuran (traces).

It was also demonstrated that, in some cases, benzamide formation may occur even in the absence of *t*-AmONa. Thus, a particularly striking reaction was observed with piperidine (Scheme I).

However this reaction seems to be restricted to sufficiently nucleophilic and basic amines; indeed, no reaction occurred when diethylamine was used instead of piperidine.

Finally, the possible catalytic preparation of benzamides was examined. As expected, these carbonylations were easily achieved by using cobalt salt in catalytic amounts (see Table V).

Conclusion

The present work confirms the versatility of MCRA. CoCRACO provides a new and very efficient system for the catalytic carbonylation of aryl halides at atmospheric pressure. New fields of applications are thus opened which are currently under study in our laboratory.

Table V. Catalytic Carbonylation of C_6H_5Br by CoCRACO in the Presence of Amines

$$C_6H_5Br \xrightarrow[\text{(2) } H_3O^+]{\text{(1) NaH-}t\text{-AmONa-amine-Co(OAc)}_2{}^a\text{-CO, THF,}^b\ 63\ ^\circ\text{C}} C_6H_5CON< + C_6H_5COO\text{-}t\text{-Am} + C_6H_5COOH^c$$

amine	reaction time, h	% recovered[d] C_6H_5Br	% reduction[d] to C_6H_6	amide[e] yield, %	ester[e] yield, %	acid[e] yield, %	overall carbonylation yield with respect to cobalt
c-$C_6H_{11}NH_2$	35	5	15–20	55–60	0–5	5–10	350–375
Et_2NH	60	5	35–40	40–45	0–5	0–5	225–250
$C_5H_{11}N$	25	5	10–15	50–55	5–10	10–15	350–375[f]

[a] NaH/*t*-AmONa/amine/Co(OAc)$_2$/C_6H_5Br = 100/20/100/10/50 mM. [b] 50 mL. [c] In all cases 2-phenyltetrahydrofuran was formed in 5–10% yield. [d] Determined by GLC analysis with internal standards. [e] Isolated yields based upon starting C_6H_5Br (50 mM). [f] Benzaldehyde was formed in 5% yield with respect to C_6H_5Br.

Experimental Section

Materials. Fluka sodium hydride (55–60% in oil) was used and washed several times with THF. Badische Anilin reagent grade THF was distilled from benzophenone–sodium couple just before use (the absence of peroxides was tested before each run). Aryl halides (Fluka or Aldrich) were purified by distillation. Alcohols (Fluka or Aldrich) were distilled from sodium before use. Cobalt acetate (Prolabo) was dried under vacuum for 12–15 h at 80–100 °C. Argon U and carbon monoxide (N 20, L'Air Liquide) were used. Silica column chromatographies were performed using Kieselgel Merck (0.063–0.200 mm).

General. GLC analyses were performed on a Girdel 75 CD/PT apparatus equipped with 5 m (15%) SE 30 columns. Infrared spectra were recorded with a Perkin-Elmer 457 spectrometer and NMR spectra with a Perkin-Elmer R 12 instrument.

General Carbonylation Procedure (Table I). All experiments were carried out under a well-ventilated hood. The general procedure is exemplified for the carbonylation of bromobenzene by NaH-*neo*-PeONa–Co(OAc)$_2$–CO. Neopentyl alcohol (20 mM) in THF (10 mL) was added dropwise to a suspension of NaH (60 mM) in gently refluxing THF (25 mL) under an argon atmosphere. After having been stirred for 1 h, the reaction medium was cooled to room temperature, and argon was replaced by carbon monoxide (measured flow rate: 2 L/h). Then, cobalt acetate (10 mM) was added. A blue color rapidly developed. After the mixture was stirred for 2 h under CO at room temperature, bromobenzene (20 mM) and the internal standard (decane) in THF (15 mL) were added, and the flask was warmed to 63 °C with an oil bath. The carbon monoxide stream was continued throughout the reaction. Small aliquots were removed periodically through a septum cap, acidified by dilute HCl, and extracted with diethyl ether. The disparition of bromobenzene was monitored by GLC analysis. Upon completion of the reaction (20 h), the reaction medium was cooled, poured onto ice, acidified with dilute HCL, and extracted with diethyl ether. Classical separations led to neopentyl benzoate (73%), benzoic acid (12%), and small amounts of side reaction products as indicated in the text. For the preparation of amides, the corresponding amine (40 mM) was introduced together with the activating alcohol (*t*-AmOH). The course of the reaction was monitored as above, and classical work up was used.

Aromatic acids, aromatic amides, and formamides were identified by comparison of their physical and spectroscopic properties with those described in the literature. Aromatic esters were identified on the basis of their spectroscopic properties and saponification to the corresponding acids or by comparison with authentic samples prepared by classical procedures. 2-Phenyltetrahydrofuran, biphenyl, and benzil were identified by comparison with authentic samples.

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Registry No.—MeONa, 124-41-4; EONa, 141-52-6; *neo*-PeONa, 3561-85-1; 1-OcONa, 17158-60-0; CHexONa, 22096-22-6; 2-OcONa, 68488-95-9; *t*-AmONa, 14593-46-5; *t*-BuONa, 865-48-5; allylONa, 20907-32-8; C_6H_5Br, 108-86-1; C_6H_6, 71-43-2; C_6H_5COOH, 65-85-0; $C_6H_5COOCH_2CH_3$, 93-89-0; $C_6H_5COOCH_2C(Me)_3$, 3581-70-2; $C_6H_5COO(CH_2)_7CH_3$, 94-50-8; $C_6H_5COOC_6H_{11}$, 2412-73-9; $C_6H_5COOCH(CH_3)(CH_2)_5CH_3$, 6938-51-8; $C_6H_5COOC(Me)_2Et$, 6963-55-9; $C_6H_5COOC(Me)_3$, 774-65-2; C_6H_5Cl, 108-90-7; C_6H_5I, 591-50-4; *o*-MeC_6H_4Br, 95-46-5; *m*-MeC_6H_4Br, 591-17-3; *p*-MeC_6H_4Br, 106-38-7; *o*-$MeOC_6H_4Br$, 578-57-4; *m*-$MeOC_6H_4Br$, 2398-37-0; *p*-$MeOC_6H_4Br$, 104-92-7; *p*-FC_6H_4Br, 460-60-4; *p*-$MeCOC_6H_4Br$, 99-90-1; *p*-$Me_2NC_6H_4Br$, 586-77-6; MeC_6H_5, 108-88-3; $MeCOC_6H_5$, 98-86-2; Me_2NC_6Hr, 121-69-7; *o*-MeC_6H_4COOH, 118-90-1; *m*-MeC_6H_4COOH, 99-04-7; *p*-MeC_6H_4COOH, 99-94-5; *o*-$MeOC_7H_4COOH$, 579-75-; *m*-$MeOC_6H_4COOH$, 586-38-9; *p*-MeO-C_7H_4COOH, 100-09-4; *p*-FC_6H_4COOH, 456-22-4; *p*-MeCO-C_6H_4COOH, 586-89-0; *p*-$Me_2NC_6H_4COOH$, 619-84-1; *o*-Me-$C_6H_4COOCH_2C(Me)_3$, 69911-99-5; *m*-$MeC_6H_4COOCH_2C(Me)_3$, 69912-00-1; *p*-$MeC_6H_4COOCH_2C(Me)_3$, 69912-01-2; *o*-MeO-$C_7H_4COOCH_2C(Me)_3$, 66702-44-1; *m*-$MeOC_6H_4COOCH_2C(Me)_3$, 69912-02-3; *p*-$MeOC_6H_4COOCH_2C(Me)_3$, 3581-72-4; *p*-$FC_6H_4COOCH_2C(Me)_3$, 69912-03-4; *p*-$MeCOC_6H_4COOCH_2C(Me)_3$, 69912-04-5; *p*-$Me_2NC_6H_4COOCH_2C(Me)_3$, 69912-05-6; *r*-$C_4H_9NH_2$, 109-73-9; *n*-$C_8H_{17}NH_2$, 111-86-4; c-$C_6H_{11}NH_2$, 108-91-8; Et_2NH, 109-89-7 (*i*-Pr)$_2$NH, 108-18-9; $C_5H_{11}N$, 110-89-4; HCONHBu, 871-71-6; HCONH(*n*-C_8H_{17}), 6282-06-0; C_6H_5CONH(c-C_6H_{11}), 1759-68-8; $C_6H_5CONEt_2$, 1696-17-9; C_6H_5CON(*i*-Pr)$_2$, 20383-28-2; CO, 630-08-0; Co(OAc)$_2$, 71-48-7; NaH, 7646-69-7; *N*-benzoylpiperidine, 27457-29-0; 2-phenyltetrahydrofuran, 16133-83-8.

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