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ACTIVATION OF REDUCING AGENTS. SODIUM HYDRIDE CONTAINING COMPLEX REDUCING AGENTS

XIV *. $NaCoCO_4$ AS AN $S_{RN}1$ NUCLEOPHILE IN THE CARBONYLATION OF ARYL HALIDES BY CoCRACO AT ATMOSPHERIC PRESSURE. NEW PREPARATION OF $NaCoCO_4$ BY NaH REDUCTION OF DICOBALT OCTACARBONYL

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Summary

The only detectable cobalt carbonyl species present in CoCRACO (NaH/t-AmONa/Co(OAc)$_2$/CO) (t-Am = tert-amyl) is $NaCoCO_4$. The simultaneous presence of NaH, t-AmONa, $NaCoCO_4$ and some soluble, non-carbonyl, cobalt species allows highly catalytic carbonylation of C_6H_5Br under very mild conditions, while $NaCoCO_4$ alone can carbonylate C_6H_5Br under irradiation (350 nm). In the presence of t-AmONa, the reaction is highly catalytic with respect to cobalt. These results strongly suggest a $S_{RN}1$ mechanism. It is suggested that catalytic carbonylations with CoCRACO take place by a $S_{RN}1$, electron-initiated, reaction. A new, very convenient method of preparation of $NaCoCO_4$ by quantitative reduction of Co_2CO_8 with NaH is also described.

Introduction

Since our first reports [2] on the reducing properties of commercial sodium hydride on organic compounds, we have considerably developed the applications of this cheap and very easily handled reagent. First, we have demonstrated that the reducing properties of NaH can be enhanced by sodium alkoxides [3] as can be basic properties of sodamide in complex bases [4]. Further, we found that addition of transition metal salts to NaH/RONa mixtures led to interesting reducing agents, which we called complex reducing agents (CRA) [5]. As an

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* For part XIII see ref. 1.

extension of the known applications of CRA (catalytic chemical reduction of organic halides [5] and ketones [6], highly selective reduction of $\alpha\beta$-unsaturated ketones [7], preparation of very efficient heterogeneous hydrogenation catalysts [8]) the possibility that the system, "NaH/RONa/Co(OAc)$_2$/CO" (referred to as CoCRACO) might allow atmospheric pressure catalytic carbonylation of aryl halides was particularly interesting (Scheme 1).

SCHEME 1

$$\mathrm{ArX} \xrightarrow[\text{2) } H_3O^+]{\text{1) ``NaH/RONa/Co(OAc)}_2\text{/CO'', THF}} \mathrm{ArCOOH + ArCOOR}$$

$X = Cl, Br, I$

The synthetic usefulness of CoCRACO has been described in a previous publication [9]. However, the observed reactions raised an intriguing question, since no atmospheric pressure carbonylation of aryl halides by a cobalt carbonyl species has ever been reported [10]. Thus, the identity of the actual nature of the active species in CoCRACO presented an interesting problem, and we describe below the results of our investigations on this point.

We shall see that CoCRACO does not involve a new cobalt carbonyl species, but rather a new reaction system. The carbonylating species, is in fact, $NaCoCO_4$, but the reaction is made possible only by the presence of sodium hydride and alkoxides. Incidentally, we also describe a new, very easy method of preparation of $NaCoCO_4$ by quantitative NaH reduction of Co_2CO_8 in THF.

Results and discussion

Study of CoCRACO; reactivity of the NaH/t-AmONa/NaCoCO$_4$ system

As mentioned above, no atmospheric pressure carbonylation of aryl halides by known carbonyl species has ever been reported [10]. Thus, carbonylations performed with CoCRACO could be interpreted in one of two ways: (a) formation of some new, very active cobalt carbonyl species, and (b) formation of classical species in a reaction system allowing their reaction with aryl halides.

In order to decide between these possibilities, we carried out a thorough study of CoCRACO.

First of all, since CoCRACO is a heterogeneous reagent, it was necessary to determine in which phase the cobalt was located. Addition of Co(OAc)$_2$ to a NaH/t-AmONa mixture in THF under 1 atm carbon monoxide (see Experimental) followed by centrifugation and cobalt titration led to the following observations:

(i) After stirring for 2 h at 25°C, about 70% of the cobalt was located in the liquid phase.

(ii) After stirring for 2 h at 25°C, and 2 additional hours at 63°C (which is the usual carbonylation temperature) about 90% of the cobalt was in solution.

The liquid phase obtained after 2 h at 25°C was not able to carbonylate C_6H_5Br but did so (200% yield with respect to cobalt after 24 h at 63°C under 1 atm carbon monoxide) in the presence of added NaH.

Taking into account the fact that the solid phase exhibited no IR carbonyl absorptions in the 2500–1600 cm^{-1} region, we formulated the preliminary hypothesis that one or several soluble active carbonyl species were formed from the starting reagents accumulated in the solid phase. In agreement with this, we observed that the solid phase after being placed again in THF and stirred for a further 1 h under carbon monoxide (see Experimental) was able to carbonylate C_6H_5Br (85% yield with respect to cobalt after 24 h at 63°C).

In the light of these results we decided to study the IR spectra of the liquid phases obtained by reaction of $Co(OAc)_2$ with either NaH, or t-AmONa or NaH/t-AmONa under carbon monoxide. Table 1 lists the IR spectral data for the solutions as well as carbonylation data for each complete system. It is noteworthy that the only carbonyl absorptions observed in the 2500–1600 cm^{-1} region correspond to those described for $NaCoCO_4$ in THF [11]. These results also confirm (vide supra) that carbonylation of C_6H_5Br requires the presence of both this carbonyl species and sodium hydride.

The presence of $NaCoCO_4$ was further confirmed by treating the liquid phase of CoCRACO with $(C_6H_5)_3SnCl$ to give $(C_6H_5)_3SnCoCO_4$, identified by comparison with an authentic sample [12]. Classical titration of $NaCoCO_4$ [13] present in the liquid phase after 2 h preparation at 25°C indicated the presence of about 0.6 to 0.8 mmol of this species. Heating to reflux for 2 hours more led to a maximum of 1.2 mmol, although 90% of the cobalt (i.e. 9 mmol) went into solution. It was not possible to exceed this amount of $NaCOCO_4$. On the other hand, direct destruction of soluble carbonyl species in CoCRACO by an iodine/potassium iodide solution [13] led to the same carbon monoxide release as that obtained by destruction of the preformed $[Ni(phen)_3](CoCO_4)_2$ complex [13], showing that $NaCoCO_4$ was the only carbonyl species in CoCRACO [14].

These observations led us to conclude that $NaCoCO_4$ was the actual carbonylating species in CoCRACO. However, it is well established [10,15] that this metal carbonyl anion cannot carbonylate C_6H_5Br under such mild conditions. Thus, in the light of the results listed in Table 1, it seemed likely that the presence of NaH (and maybe of t-AmONa) was responsible for the observed carbonylations. In order to clarify this point, we prepared $NaCoCO_4$ by Na/Hg reduction of Co_2CO_8 and studied its reactivity toward C_6H_5Br in the presence of either NaH or t-AmONa or NaH/t-AmONa (the possible influence of AcONa was also tested, and this salt found to have no observable effect). The main results are summarized in Table 2. It should be noted that although the experimental procedure was the same as for the CoCRACO carbonylations, the $NaCoCO_4$ concentration was much higher in each case studied here. Nevertheless, even in the most favourable case, the carbonylation yield was not higher than those obtained with CoCRACO [9].

As expected from earlier work [15], $NaCoCO_4$ gave no carbonylation in the absence of other reagents. It is noteworthy that the presence of sodium hydride promotes carbonylation and that the simultaneous presence of t-AmONa enhances the activity even more (although the t-AmONa/$NaCoCO_4$ mixture (20/10 mmol) was not efficient for the carbonylation).

The above observations bring to mind the enhancing effect of sodium alkoxides on the electron donor properties of NaH in THF [3].

It has been previously demonstrated that the cobalt complex reducing

TABLE 1

IR ABSORPTION AND CARBONYLATING ABILITIES OF REAGENTS OBTAINED BY REACTION OF $Co(OAc)_2$ WITH NaH, t-AmONa or NaH/2-AmONa UNDER CARBON MONOXIDE (1 atm)

Reagent [a] (mmol)	IR absorption [b, c] (cm^{-1})	Carbonylation of C_6H_5Br [d]				
		Recovered C_6H_5Br [e] (%)	C_6H_6 [e] (%)	C_6H_5COOH [f] (%)	C_6H_5COO-t-Am [f] (%)	Overall carbonylation yield with respect to cobalt (%)
NaH/$Co(OAc)_2$ (60/10)	none	90—95	5	—	—	—
t-AmONa/$Co(OAc)_2$ (20/10)	1890(sh), 1885, 1855(0.1)	100	—	—	—	—
NaH/t-AmONa/$Co(OAc)_2$ (40/20/10) CoCRACO	1890(sh), 1885, 1855(1)(g)	5	10—15	45—50	15—20	120—130

[a] Reagents obtained after 2 h stirring of the components at RT under CO atmosphere in 45 ml THF. [b] IR spectra recorded in the 2500—1600 cm^{-1} region with a 0.05 mm cell on the THF solutions obtained 5 min after stirring was stopped. In all case, IR bands were observed in the 1580—1595 cm^{-1} region, assigned to carboxylate ions, as demonstrated by control experiments. [c] Estimated relative intensities in parenthesis. [d] Reactions performed on 20 mmol C_6H_5Br for 24 h in 50 ml refluxing THF under CO. [e] Determined by GLC analysis with internal standards. [f] Isolated yields with respect to C_6H_5Br. [g] Titration of $NaCoCO_4$ indicated this absorption intensity corresponded to about 0.6—0.7 mmol $NaCoCO_4$ in the reaction medium.

TABLE 2

CARBONYLATION OF C_6H_5Br (20 mmol) BY $NaCoCO_4$ (10 mmol) IN THE PRESENCE OF ADDITIONAL REAGENTS UNDER CARBON MONOXIDE (1 atm) [a]

Added reagents (mmol) [b]	Recovered C_6H_5Br (%) [c]	Reduction to C_6H_6 (%) [c]	C_6H_5COOH (%) [d]	C_6H_5COOt-Am (%) [d]	Overall carbonylation yield with respect to cobalt (%)
none	100	—	—	—	—
NaH (60)	60—65	5—10	25—30	—	55—60
t-AmONa (20)	95	traces	traces	traces	2—5
NaH/t-AmONa (40/20)	25—30	5—10	35—40	20—25	125—130
NaH/t-AcONa (60/20)	60—65	5—10	25—30	—	55—60
t-AmONa/AcONa (20/20)	100	—	—	—	—
AcONa (20)	100	—	—	—	—
NaH/t-AmONa/AcONa (40/20/20)	25—30	5—10	35—40	20—25	125—130

[a] Reactions performed for 24 h in refluxing THF. [b] $NaCoCO_4$ (10 mmol) was stirred for 2 h at RT in the presence of the added reagent(s) under CO before adding bromobenzene and heating to 63°C. [c] Determined by GLC analysis with internal standards. [d] Isolated yields with respect to C_6H_5Br.

agent "CoCRA" ($NaH/RONa/Co(OAc)_2$ system prepared under nitrogen or argon) brings about reduction of aryl halides and that free radical mechanisms might operate in reductions by CRA [5]. Thus, the carbonylation of aryl halides by $NaCoCO_4$ under mild conditions could be due to the operation of a free radical rather than an ionic mechanism.

Indeed, the general $S_{RN}1$ [16] mechanism pictured in Scheme 2 offers a good interpretation of the observed reactions:

SCHEME 2

$$[\text{Electron source}] + ArX \rightarrow [ArX]^{\cdot-}$$

$$[ArX]^{\cdot-} \rightarrow Ar^{\cdot} + X^-$$

$$Ar^{\cdot} + CoCO_4^- \rightarrow [ArCoCO_4]^{\cdot-}$$

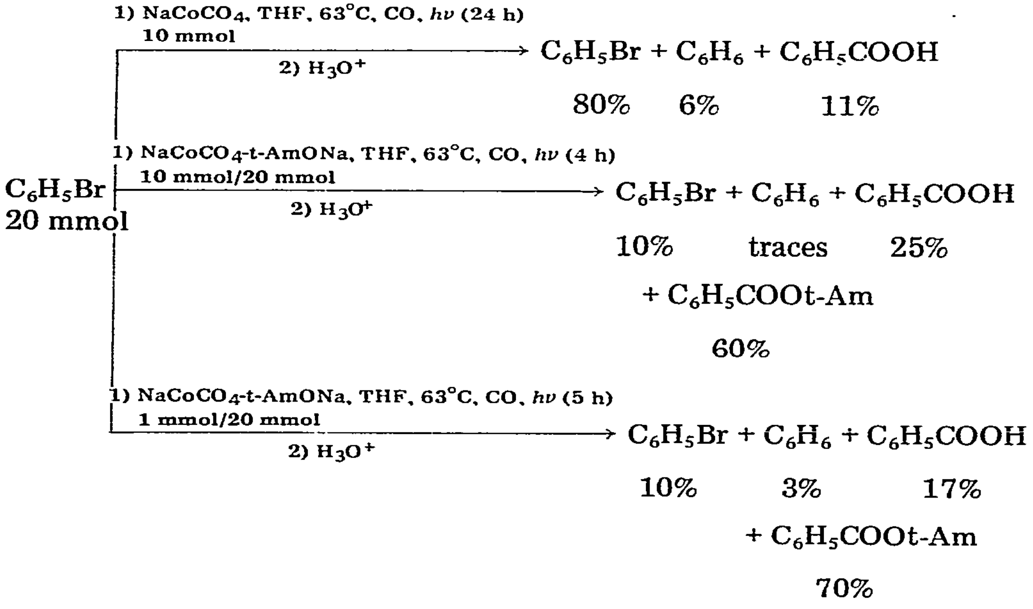
$$[ArCoCO_4]^{\cdot-} + ArX \rightarrow \underset{\substack{\downarrow \\ \text{carbonylation} \\ \text{products}}}{ArCoCO_4} + \underset{\substack{\downarrow \\ \text{propagation}}}{[ArX]^{\cdot-}}$$

We cannot specify the actual nature of the electron source, but from Table 2 it seems that NaH certainly plays an important role in the initiation step.

Taking into account what is known about $S_{RN}1$ [16] condensations, and the electron donor ability of $CoCO_4^-$ [17] we might expect to observe photostimulated reactions of $NaCoCO_4$ with C_6H_5Br. Thus, we examined the following photostimulated (350 nm) reactions (Scheme 3).

SCHEME 3

(Yields given with respect to C_6H_5Br)



The results deserve some comments. First of all, to the best of our knowledge, these reactions constitute the first example of photostimulated carbonylation of C_6H_5Br by $NaCoCO_4$. It is also clear that the presence of a nucleophile, such as t-AmONa, is needed to achieve catalytic carbonylations (yields up to about 1800% with respect to cobalt may be obtained; third experiment, Scheme 3). By analogy with the general $S_{RN}1$ mechanism described by Bunnett [6], photostimulated carbonylation of C_6H_5Br may be formulated as pictured in Scheme 4. The possibility of $NaCoCO_4$ dissociating, under $h\nu$ irradiation, to $CoCO_3^-$ followed by C_6H_5Br oxidative addition cannot be entirely excluded. However, generally speaking, such dissociations are strongly inhibited by a carbon monoxide atmosphere [18] and thus are believed not to be involved under our experimental conditions.

SCHEME 4

Initiation step

$$C_6H_5Br + NaCoCO_4 \rightleftharpoons C_6H_5Br, NaCoCO_4 \xrightarrow{h\nu} [C_6H_5Br]^{-}Na^{+} + {}^{\cdot}CoCO_4$$

$$\text{or } NaCoCO_4 \xrightarrow{h\nu} [NaCoCO_4]^{*} \xrightarrow{C_6H_5Br}$$

Propagation steps

$$[C_6H_5Br]^{-}Na^{+} \rightarrow C_6H_5^{\cdot} + NaBr$$

$$C_6H_5^{\cdot} + NaCoCO_4 \rightarrow [C_6H_5CoCO_4]^{-}Na^{+}$$

$$[C_6H_5CoCO_4]^{-}Na^{+} + C_6H_5Br \rightarrow C_6H_5CoCO_4 + [C_6H_5Br]^{-}$$

$$C_6H_5CoCO_4 + CO \rightarrow C_6H_5COCoCO_4$$

$$C_6H_5COCoCO_4 + \text{t-AmONa} \rightarrow C_6H_5COO\text{t-Am} + NaCoCO_4$$

Termination steps

$$C_6H_5CoCO_4 \rightarrow C_6H_5^{\cdot} + {}^{\cdot}CoCO_4$$

$$C_6H_5^{\cdot} + THF \rightarrow C_6H_6$$

$$C_6H_5COCoCO_4 \rightarrow C_6H_5CO^{\cdot} + {}^{\cdot}CoCO_4$$

$$C_6H_5CO^{\cdot} + THF \rightarrow C_6H_5CHO$$

Hydrolysis

$$C_6H_5COCoCO_4 + NaOH \rightarrow C_6H_5COOH + NaCoCO_4$$

$$C_6H_5COOH \xrightarrow{NaOH} C_6H_5COONa + H_2O$$

The above observation can probably be greatly extended in the field of photo- and electron-stimulated reactions of transition metal carbonyl species and we are exploring this possibility.

As to CoCRACO carbonylations, our results strongly suggest that there is electron initiated $S_{RN}1$ condensation of $NaCoCO_4$ with aryl halides. Moreover, all the side reactions observed during the CoCRACO carbonylations [9] can be explained by reactions of the termination step type. Finally, it has been reported [19,20] that $S_{RN}1$ condensations can tolerate most types of common substituents on the aromatic ring except dimethylamino, ionized hydroxy ($-O^-$) and nitro groups and it is thus relevant to note that we observed low yields for the carbonylation of *p*-(dimethylamino)bromobenzene with CoCRACO [9].

Once it was demonstrated that $NaCoCO_4$ was the active carbonyl species in CoCRACO, another question remained to be answered. As mentioned above, the liquid phase of CoCRACO contained about 90% of the starting cobalt while only 6 to 12% appeared as cobalt carbonyl species, so it was clear that the reagent prepared from NaH/t-AmONa and $NaCoCO_4$ (see Table 2) did not have the same composition as CoCRACO. Thus, we compared the catalytic properties of both reagents for the carbonylation of C_6H_5Br. As may be seen from the first two experiments in Table 3, both systems were catalytic with respect to cobalt. However, CoCRACO was more efficient, taking into account the amount of $NaCoCO_4$ formed in this reagent (vide supra). This observation led to believing that soluble non-carbonyl cobalt species play an important, but still obscure, role in the reaction. The greater efficiency of CoCRACO was further evidenced by the third experiment in Table 3. (Incidentally, we observed that, starting from 1 mmol cobalt acetate, only about 10% was transformed to $NaCoCO_4$; at the present time we have no explanation for this.) Finally, it appeared that the photostimulated carbonylation system was even more efficient than CoCRACO, but less convenient.

We conclude that CoCRACO is the most efficient reagent among the non-

TABLE 3

CATALYTIC CARBONYLATIONS OF C_6H_5Br (20 mmol) UNDER CARBON MONOXIDE (1 atm) IN REFLUXING THF [a]

Reagents (mmol)	Reaction time (h)	Overall carbonylation yield [b] (%)		Reduction to C_6H_6 (%) [c]	Recovered C_6H_5Br (%) [c]
		with respect $NaCoCO_4$	with respect to total cobalt		
NaH/t-AmONa/$Co(OAc)_2$ (40/20/10)	24	~1300 [d]	~130	15—20	5
NaH/t-AmONa/$NaCoCO_4$ (40/20/1)	24	600	600	15—20	50
NaH/t-AmONa/$Co(OAc)_2$ (40/20/1)	24	~12 500 [d]	1250	5—10	30
t-AmONa/$NaCoCO_4$ [e] (20/1)	5	1800	1800	0— 5	10

[a] 50 ml. [b] i.e. overall yield in benzoic acid, tertioamyl benzoate and benzaldehyde. [c] Determined by GLC analysis with internal standards and given with respect to C_6H_5Br. [d] Calculated with respect to the amount of $NaCoCO_4$ present in CoCRACO, i.e. about 10% of the total cobalt. [e] Under $h\nu$ (350 nm).

photostimulated systems. The special properties of CoCRACO are due to the simultaneous presence of NaH, t-AmONa, $NaCoCO_4$ and some soluble, non carbonyl, cobalt species.

Finally, we were intrigued by the problem of the formation of a CoCRACO. Obviously, it is a very difficult task to elucidate the actual route to this system from the reagents. At present we have a little relevant information as given below:

(a) Monitoring of the IR spectra of the liquid phase every thirty minutes during the preparation of a CoCRACO at 25°C then for 2 h heating at 63°C, indicated that no carbonyl absorptions other than that due to $NaCoCO_4$ appeared in the 2500—1600 cm^{-1} region.

(b) Reaction of carbon monoxide with t-AmONa/$Co(OAc)_2$ (20/10 mmol) led to $NaCoCO_4$ formation but the reaction was much slower than in the presence of NaH. To the best of our knowledge, no reaction of carbon monoxide with cobalt acetate or cobalt alkoxide has been reported, However, some examples of metal carbonyl formation [21], or metallic salt reduction [22] have been reported for the reaction of carbon monoxide with metal alkoxides. Thus, the formation of $NaCoCO_4$ may be due to the carbonylating reduction of cobalt alkoxides by carbon monoxide. During the preparation of CoCRACO, NaH must be the main electron source, thus promoting a more rapid formation of $NaCoCO_4$.

$NaCoCO_4$ can be formed from the soluble part of t-AmONa/$Co(OAc)_2$ mixtures. Thus, stirring a t-AmONa/$Co(OAc)_2$ (20/10 mmol) mixture for 2 h at 25°C under argon gave about 7 mmol of soluble cobalt species, as determined by titration after centrifugation. Reacting this liquid phase with NaH under carbon monoxide for 2 h at 25°C led to $NaCoCO_4$ generation. As cobalt acetate is only sparingly soluble in THF, these experiments suggest the formation of $NaCoCO_4$ by reduction of soluble cobalt alkoxides.

Study of Co_2CO_8. New preparation of $NaCoCO_4$

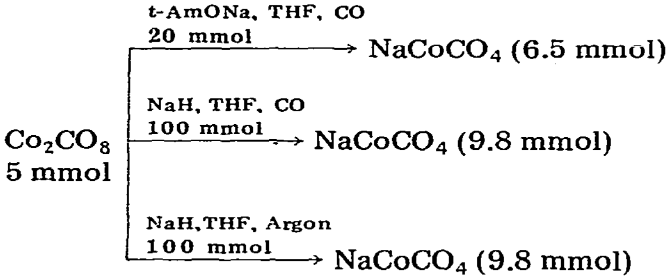
It is well known that $NaCoCO_4$ may be obtained by reduction of Co_2CO_8. The most commonly used reducing agent is a 1% Na/Hg amalgam [15,23] but other heterogeneous reductants such as Na/K alloy [24] or a Na dispersion [25] can also be used. As part of our general study on the reducing properties of NaH and NaH/RONa we decided to see if it was possible to generate this useful carbonyl species by using NaH/t-AmONa as the reducing system.

The reaction performed in this way (Scheme 5) clearly indicated that, under these conditions, $NaCoCO_4$ is formed in larger amounts than expected for simple disproportionation (6.6 mmol). Thus, it was clear that some reduction occurred, and we examined the possible reactions of Co_2CO_8 with t-AmONa or NaH (Scheme 6).

SCHEME 5

$$\begin{array}{llll} \text{NaH/t-AmONa} & + \; Co_2CO_8 & \xrightarrow[\text{THF, 2 h, 25°C; 2 h, 63°C}]{\text{CO}} & NaCoCO_4 \\ \text{40 mmol} \;\; \text{20 mmol} & \;\; \text{5 mmol} & & \text{7.7 mmol} \end{array}$$

SCHEME 6



It appears that t-AmONa leads only to disporportionation. Taking into account earlier reports [10], such disporportionation in the presence of a charged base may be formulated as depicted in Scheme 7.

SCHEME 7

$$3\ Co_2CO_8 + 4\text{-t-AmONa} \rightarrow 2(\text{t-AmO})_2Co + 4\ NaCoCO_4 + 8\ CO$$

Monitoring this reaction by recording the IR spectra revealed, along with the appearance of $NaCoCO_4$, the transient formation of unknown carbonyl species exhibiting strong IR absorptions at 1955 and 1940 cm^{-1} (see Experimental).

In contrast, NaH promotes quantitative formation of $NaCoCO_4$, even under argon (see Experimental). Of course, a large excess of NaH was used, but the $NaCoCO_4$ solution could be easily syringed (or filtered). Thus, this new, very convenient preparation of $NaCoCO_4$ must be highly recommended, as it avoids the difficulties associated with earlier methods [26]. The generation of $NaCoCO_4$ may be formulated [17] as shown in Scheme 8.

SCHEME 8

$$Co_2CO_8 \xrightarrow{NaH} [Co_2CO_8]^{-}Na^{+} + H^{\cdot}$$

$$[Co_2CO_8]^{-}Na^{+} \rightarrow NaCoCO_4 + CoCO_4^{\cdot}$$

$$CoCO_4^{\cdot} + NaH \rightarrow NaCoCO_4 + H^{\cdot}$$

Finally, we briefly studied the possible carbonylation of C_6H_5Br (20 mmol) by the systems studied above (see Experimental). The main features may be summarized as follows:

(a) The t-AmONa/Co_2CO_8 system (20/5 mmol) gave about 60% carbonylation (with respect to cobalt) in 24 h. During this reaction, we made the (unexplained) observation that maximum yields were obtained only if the C_6H_5Br was added to the reaction medium when the species exhibiting the 1955 and 1940 cm^{-1} IR absorption (vide supra) were present.

(b) The NaH/Co_2CO_8 system (100/5 mmol) gave 60% benzoic acid (with respect to cobalt) after 24 h reaction.

(c) The NaH/t-AmONa/Co_2CO_8 system (40/20/5 mmol) brought about catalytic carbonylation of C_6H_5Br (160—180% with respect to cobalt). Using 0.5 mmol Co_2CO_8, yields up to 900% can be obtained in 24 h. Interestingly, we observed that the presence of sodium acetate (20 mmol) slightly increased the carbonylation rate.

Conclusion

From the present work, three main conclusions may be drawn.

First, sodium tetracarbonyl cobaltate may be generated from cobalt acetate under very mild conditions, owing to the simultaneous presence, under carbon monoxide, of NaH and sodium alkoxide. This constitutes an additional interesting application of the activation concept we have been developing for several years [4]. Although the conversion was low, generation of $NaCoCO_4$ in the presence of NaH and soluble, non carbonyl, cobalt species, among others, enables CoCRACO to bring about efficient catalytic carbonylation of C_6H_5Br. We are at present extending these concepts to other transition metals and other substrates.

Second, photostimulated, catalytic carbonylations of aryl halides by $NaCoCO_4$ are also feasible in the presence of a nucleophile. The large scope of this type of reaction is currently under investigation in our laboratory.

Finally, it is noteworthy that quantitative reduction of Co_2CO_8 to $NaCoCO_4$ may be readily achieved by use of the cheap and easily handled reagent sodium hydride.

Experimental

Materials

Fluka sodium hydride (55—60% in oil) was used and washed several times with THF under argon. Badische Anilin reagent grade THF was distilled from benzophenone/sodium couple just before use (the absence of peroxides was checked before each run). Bromobenzene (Fluka) was purified by distillation. Tert-amyl alcohol was distilled from sodium. Cobalt acetate (Prolabo) was dried under vacuum for 12—15 h at 80—100°C, as was sodium acetate (Prolabo). Co_2CO_8 (Fluka) was used without further purification. $NaCoCO_4$ was prepared by Na/Hg reduction of Co_2CO_8 following the procedure described by Seyferth [27]. U argon and N20 carbon monoxide (L'air Liquide) were used. Silica column chromatography was performed using Merck Kieselgel (0.063—0.200 mm).

General

GLC analysis were carried out with a Girdel 75 CD/PT or Girdel 300 apparatus equipped with 5 m (15%) SE 30 or UCON 50 HB 2000 columns. IR spectra were recorded with a Perkin Elmer spectrophotometer, Model 580 B. A standard 0.05 mm cavity cell and a variable path cell (micrometer type) with NaCl windows were used. Before each IR measurement, both cells were matched for THF absorption in the 1960 cm^{-1} region. Cobalt titrations were performed with a Varian Techtron Atomic Absorption photometer (Model 1200) used at 304.4 nm.

Preparation of CoCRACO. General carbonylation procedure (Table 1)

Tert-amyl alcohol (20 mmol) in THF (20 ml) was added dropwise to a stirred suspension of NaH (60 mmol) in gently refluxing THF (25 ml) under argon. After stirring for 1 h at 63°C, the mixture was allowed to cool to room temperature (25°C) and argon was replaced by a slow stream of cobalt monoxide (about 2 l/h). Cobalt acetate (10 mmol) was added (a blue color rapidly developed) and the mixture stirred for 2 h at 25°C under carbon monoxide to give to the reagent referred to as CoCRACO.

Other reagents tested (Table 1) were prepared similarly, but one component was omitted. Sodium tert-amyl oxide was prepared by reacting t-AmOH with an excess of sodium wire for 12 h in refluxing THF, then removing the residual sodium. (The IR spectra of the THF solution of t-AmONa indicated no free alcohol).

For carbonylations, bromobenzene (20 mmol) and the internal standard (undecane) in THF (5 ml) were added to CoCRACO and the reaction flask was warmed to 63°C with an oil bath. The carbon monixude stream was continued throughout the reaction. After 24 h reaction, 10 mmol toluene (internal standard for benzene determination) in THF (5 ml) was introduced, and a small aliquot was removed, acidified with dilute HCl, extracted with diethyl ether and analysed by GLC for benzene (UCON 50 HB 2000 column) and recovered bromobenzene (SE 30 column). The reaction medium was then cooled, poured onto ice, acidified with dilute HCl and extracted with diethyl ether. Conventional methods of separation gave benzoic acid, tert-amyl benzoate (after silica column chromatography with petroleum ether/ether mixtures) and, in some cases, benzaldehyde.

Separation of liquid and solid phases of CoCRACO

After CoCRACO had been obtained at 25°C, the reaction medium was centrifuged (Janetzki Model T 32, about 1000 g) for 30 min.

The liquid phase (which IR spectra exhibited only $NaCoCO_4$ absorptions), replaced under a CO atmosphere, did not react with bromobenzene after 24 h at 63°C. However, in the presence of added NaH (60 mmol), the liquid phase did carbonylate bromobenzene (20 mmol) to yield, after 24 h at 63°C under CO: 25% recovered C_6H_5Br, 10% benzene, 10% benzoic acid and 50% tertioamyl benzoate (yields with respect to bromobenzene). Cobalt titration indicated this phase contained 6 mmol cobalt.

The solid phase, the IR spectrum (Nujol) of which exhibited only carboxylate ion absorptions near 1580 cm^{-1}, was further washed several times with THF, then was placed again in 50 ml THF and stirred for 1 h under CO (after this time IR spectra of the solution indicated $NaCoCO_4$ formation). Bromobenzene (20 mmol) was then added. After 24 h at 63°C under carbon monoxide, conventional procedures yielded: 77% recovered C_6H_5Br, 5% benzene, 10% benzoic acid and 3% tert-amyl benzoate (yields with respect to C_6H_5Br). Cobalt titration indicated this phase contained 3 mmol cobalt.

Titrations of soluble cobalt species in CoCRACO

Titration of $NaCoCO_4$ present in CoCRACO was carried out on the solution obtained after centrifugation (vide supra). Direct titration of carbonyl species by destruction with a I_2/KI solution or indirect titration using $[Ni(phen)_3](CoCO_4)_2$ were performed as described by Sternberg, Wender and Orchin [13].

Titration of soluble cobalt was also carried out on the solution obtained after centrifugation. The usual treatment with nitric acid led to Co^{2+} solutions which were titrated using atomic absorption spectroscopy.

Carbonylations by $NaCoCO_4$ containing systems (Table 2)

For each system, $NaCoCO_4$ and the additional reagent(s) were stirred for 2 h at 25°C in 50 ml THF under carbon monoxide. In each case the IR spectra of the solutions obtained exhibited only $NaCoCO_4$ IR absorptions. Carbonylations were then conducted as described above for Table 1 experiments.

Photostimulated carbonylations of bromobenzene (Scheme 3)

Photostimulated carbonylations were carried out using the general procedure described above, in Pyrex flasks irradiated by 350 nm ultraviolet lamps in a Rayonnet photochemical reactor, as described by Bunnett [28]. Heating to 63°C was achieved by means of a 60 W tungsten lamp placed under the reaction flask. The irradiation and the carbon monoxide stream were maintained throughout the reaction.

Preparation of $NaCoCO_4$ by NaH reduction of Co_2CO_8 (Scheme 6)

Co_2CO_8 (5 mmol) was added to a stirred suspension of NaH (100 mmol) in THF (50 ml) under argon. After 2 h at 25°C the temperature was raised to 63°C with an oil bath for 2 more hours. The $NaCoCO_4$ solution was then syringed (or filtered) after decantation. IR measurement and $NaCoCO_4$ titration indicated quantitative transformation (98%).

Carbonylations by systems generated from Co_2CO_8 (Table 3)

Co_2CO_8 (5 mmol) was added to the coreagent(s) i.e. either t-AmONa (20 mmol) or NaH (100 mmol) or NaH/t-AmONa (40/20 mmol) in 50 ml THF and stirred for 2 h at 25°C under carbon monoxide. At this time, IR spectra of the solutions were recorded. The t-AmONa/Co_2CO_8 and NaH/t-AmONa/Co_2CO_8 systems exhibited both $NaCoCO_4$ absorptions (1885 and 1855 cm^{-1}) and unassigned carbonyl bands at 1955 and 1940 cm^{-1}; in each case these latter bands were shown to disappear after 2 h heating at 63°C. The NaH/Co_2CO_8 system exhibited both $NaCoCO_4$ bands and small Co_2CO_8 bands (which were shown to disappear on further 2 h heating at 63°C).

The bromobenzene carbonylations were then conducted as described above.

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