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# STOICHIOMETRIC HYDRODEHALOGENATION AND FORMYLATION OF ORGANIC HALIDES USING TETRACARBONYL COBALTATE(—I)

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## Summary

Methanolic solutions of tetracarbonyl cobaltate(—I) in the presence of an acid bring about replacement of organic halogens by hydrogen or the formyl group. In general, hydrogenolysis is the main (often the only) reaction, but formylation becomes significant with aliphatic and benzyl halides.

## Introduction

The reaction between organic halides and $[Co(CO)_4]^-$ has been used for the preparation of carboxylic acids [1—3], esters [4], lactones [5—7], amides [4] and ketones [8—9]. We now describe a procedure by which an organic halogen can be replaced by hydrogen or a formyl group using the tetracarbonyl cobaltate anion as reagent.

## Results and discussion

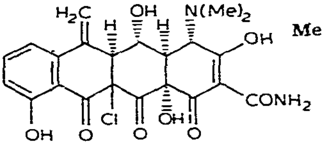
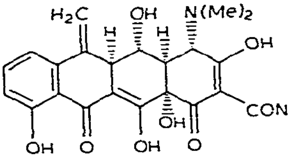
As we reported earlier [10] the methanolic or ethanolic solution of $Co_2(CO)_8$ can be regarded as containing $[Co(CO)_4]^-$ and $CoH(CO)_4$ and in the presence of a mineral acid (such as hydrochlorid acid) it brings about hydrogenation of conjugated olefinic double bonds. We have now found that this reagent is effective for the hydrodehalogenation of various organic halogen compounds under ambient conditions. The reaction has the following stoichiometry:

$$3 \geqslant C-X + 2[Co(CO)_4]^- + 3\,H^+ \rightarrow 3 \geqslant C-H + 2\,Co^{2+} + 3\,X^- + 8\,CO$$

The presence of an acid is essential for rapid reaction: under neutral conditions the hydrogenolysis is very slow, while under basic conditions catalytic alkoxy carbonylation occurs [8]. The yield of the hydrogenated products and

TABLE 1

STOICHIOMETRIC HYDROGENOLYSIS OF ORGANIC HALIDES USING SOLUTIONS OF $[Co(CO)_4]^-$ AT 25°C UNDER CO [a]

| Substrate | Solvent [b] | Reaction time (min) | Product | Yield [c] (%) |
|---|---|---|---|---|
| $Ph_3CCl$ [d] | MeOH | 5 | $Ph_3CH$ | 99 [e] |
| $PhCH_2Cl$ | MeOH | 300 | $PhCH_3$ | 12 |
| | | | $PhCH_2CHO$ | 25 [f] |
| PhCOCl | $MeOCH_2CH_2OMe$ | 30 | PhCHO | 10 |
| PhCl | MeOH | 180 | PhH | 4 |
| PhI | MeOH | 360 | PhH | 5 |
| $4\text{-}MeOC_6H_4Br$ | MeOH | 360 | MeOPh | 7 |
| $CH_3I$ | MeOH | 600 | $CH_3CHO$ | 38 [f] |
| $CBr_4$ | MeOH | 2 | $CHBr_3$ | 90 |
| $CHBr_3$ | MeOH | 240 | $CH_2Br_2$ | 22 |
| $CCl_4$ | MeOH | 20 | $CHCl_3$ | 27 |
| $EtOOCCH_2Br$ | EtOH | 7 | $EtOOCCH_3$ | 100 |
| $EtOOCCH_2Cl$ | EtOH | 360 | $EtOOCCH_3$ | 58 |
| $MeOOCCHCl_2$ | MeOH | 180 | $MeOOCCH_2Cl$ | 64 |
| $MeOOCCH_2CH_2Br$ | MeOH | 360 | $MeOOCCH_2CH_3$ | 2 |
| $EtOOCCHBrCH_3$ | EtOH | 30 | $EtOOCCH_2CH_3$ | 98 |
| $EtOOCCHBrCH_3$ | EtOD [g] | 30 | $EtOOCCHDCH_3$ [h] | 98 |
| $EtOOCCBr(CH_3)CH_3$ | EtOH | 60 | $EtOOCCH(CH_3)CH_3$ | 97 |
|  | MeOH | 30 |  | 94 [i] |

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[a] 1.5 mol HCl and 1.5 mol substrate for each mol of $[Co(CO)_4]^-$. [b] 2—5 ml solvent/mmol substrate and 2—5 ml solvent/mmol $[Co(CO)_4]^-$. [c] based on GLC analysis using internal standards; [d] substrate dissolved in benzene; [e] product isolated; [f] product isolated as 2,4-dinitrophenylhydrazone and identified by $^1H$ NMR; [g] 20% DCl in $D_2O$ was used as acid component; [h] product composition was determined by GLC-MS analysis; [i] product isolated as sulphosalicylate adduct.

the rate of the reaction depend markedly on the structure of the organic halide, as shown in Table 1.

The hydrogenolysis of the carbon—halogen bond is often accompanied by aldehyde formation. In such cases CO absorption can be observed in the early stages of the reaction. Yields of formylated products are somewhat higher if the acid is added only after the absorption of CO has ended. Examples of aldehyde yields under such experimental conditions are given in Table 2.

The results may be interpreted in terms of the following reaction scheme:

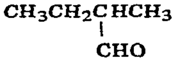
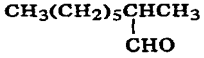
$$Co_2(CO)_8 \xrightarrow{CH_3OH} [Co(CH_3OH)_6][Co(CO)_4]_2$$

$$[Co(CO)_4]^- + H^+ \rightleftharpoons CoH(CO)_4$$

$$\begin{tikzcd}
R\text{—}X \arrow[r, "{[Co(CO)_4]^-}"] & R\text{—}Co(CO)_4 \arrow[r, "CoH(CO)_4", "(a)"'] \arrow[d, "(b)"', "CO"] & R\text{—}H + Co_2(CO)_8 \\
 & R\text{—}\underset{\overset{\|}{O}}{C}\text{—}Co(CO)_4 \arrow[r, "CoH(CO)_4"] & R\text{—}CHO + Co_2(CO)_8
\end{tikzcd}$$

TABLE 2

FORMATION OF ALDEHYDES FROM ORGANIC HALIDES BY TREATMENT WITH $[Co(CO)_4]^-$ IN METHANOL UNDER CO FOLLOWED BY ACIDIFICATION [a]

| Substrate | Reaction time [b] (hours) | Temp. (°C) | Products | Yield [c] (%) |
|---|---|---|---|---|
| $CH_3I$ | 1 + 9 | 12 | $CH_3CHO$ | 55 |
| $CH_3I$ | 0.3 + 1.6 | 25 | $CH_3CHO$ | 57 |
| $CH_3I$ [d] | 1 + 8 | 12 | $CH_3CDO$ | 48 |
| $CH_3CH_2I$ | 12 + 4 | 25 | $CH_3CH_2CHO$ | 46 |
| $CH_3(CH_2)_3I$ | 20 + 4 | 25 | $CH_3(CH_2)_3CHO$ | 18 |
| | | |  $CH_3CH_2\underset{CHO}{\underset{\mid}{C}}HCH_3$ | 13 |
| $CH_3(CH_2)_7I$ | 48 + 5 | 25 | $CH_3(CH_2)_7CHO$ | 29 |
| | | |  $CH_3(CH_2)_5\underset{CHO}{\underset{\mid}{C}}HCH_3$ | 18 |
| | | | $CH_3(CH_2)_6CH_3$ | 1 [e] |
| $MeOOCH_2CH_2Br$ | 50 + 5 | 25 | $MeOOCCH_2CH_2CHO$ | 38 |
| | | | $MeOOCCH_2CH_3$ | 12 [e] |
| $PhCH_2Cl$ | 6 + 3 | 25 | $PhCH_2CHO$ | 43 |
| | | | $PhCH_2CH_2OH$ | 8 [e] |
| | | | $PhCH_3$ | 28 [e] |

[a] 1.5 mol HCl/mol $[Co(CO)_4]^-$, 1.5 mol substrate/mol $[Co(CO)_4]^-$, 1 ml methanol/mmol substrate and 1 ml methanol/mmol $[Co(CO)_4]^-$. [b] The first figure refers to the time after which CO absorption ceased, the second figure refers to the time after which CO evolution ceased after acidification. [c] Aldehydes isolated as 2,4-dinitrophenylhydrazones and identified by $^1H$ NMR. [d] $CH_3OD$ and 20% DCl in $D_2O$ was used. [e] Based on GLC analysis using internal standards.

The ratio of hydrogenated to formylated products obviously depends on the relative rates of reactions a and b. It is noteworthy that electron withdrawing substitutents of group R apparently favour the hydrogenolysis step (a) as opposed to CO insertion (b). This result is in qualitative agreement with the trend of rates of CO insertion into C—Mn and C—Fe bonds as determined by Pruett [11].

In agreement with literature reports [12], some hydrogenation of the aldehyde to alcohol was observed as a secondary reaction (cf. Table 2).

## Experimental

### *Triphenylmethane from trityl chloride*

280 mg (0.82 mmol) $Co_2(CO)_8$ and 2 ml methanol was stirred for 2 hours at 25°C until the CO evolution ceased. To the pink coloured solution 457 mg (1.64 mmol) trityl chloride in 1.5 ml benzene and 60 mg HCl (1.64 mmol) in 1.5 ml methanol was added dropwise. The rapid CO evolution ceased after 5 min, and a blue solution containing a white precipitate resulted. The mixture was poured into water and extracted with petroleum ether. The organic layer was dried and evaporated in vacuo. The residue was triphenylmethane (394 mg; 99%), m.p.: 94°C.

### *Stoichiometric hydrogenolysis of ethyl 2-bromopropianate (general procedure)*

362 mg (1.06 mmol) $Co_2(CO)_8$ and 5 ml ethanol were stirred for 30 min at 35°C. To this mixture 384 mg (2.12 mmol) ethyl 2-bromopropionate, 0.08 ml toluene (as internal standard) and 0.178 ml (2.12 mmol) conc. HCl dissolved in 5 ml EtOH was added at 25°C. After 30 min the CO evolution ceased and a blue solution resulted. Analysis by GLC (5 m 3% OV-25 on Chromosorb WHP 100/120 mesh at 120°C, FID) showed 98% conversion to ethyl propionate.

### *Stoichiometric hydrogenolysis of 11a-chloro-6-demethyl-6-desoxy-6-methylene-5-hydroxytetracycline-tosylate*

The slurry of 752 mg (2.2 mmol) $Co_2(CO)_8$ and 15 ml methanol was added in small portions with stirring to a suspension of 2.6 g (4.0 mmol) of 11a-chloro-6-demethyl-6-desoxy-6-methylene-5-hydroxytetracycline-tosylate in 20 ml methanol containing 160 mg (4.4 mmol) HCl at room temperature. During the addition of the reagent rapid CO evolution took place, but ceased completely after additional stirring for 30 min. Following this, 1930 mg (8.0 mmol) sulphosalicyclic acid was added and the mixture was diluted with 500 ml water. The yellow crystalline solids were filtered and washed with water. After drying in vacuo, 2.5 g (94.4% yield) practically pure 6-methylene-6-demethyl-6-desoxy-5-hydroxy-tetracycline sulfosalicylate were obtained (purity checked by quantitative TLC analysis).

### *Stoichiometric formylation of methyl iodide with $[Co(CO)_4]^-$ in methanol (general procedure)*

430 mg (1.257 mmol) $Co_2(CO)_8$ were dissolved in 2 ml methanol at 35°C with stirring. The CO evolution was complete in 15 minutes. To the stirred mixture at 12°C under CO, 357 mg (2.514 mmol) methyl iodide in 2.5 ml methanol was added. After 1 hour the CO absorption finished and 0.21 ml (2.52 mmol) conc. HCl was added. CO evolution started immediately and ceased only after 9 hours. The mixture was poured into 497 mg (2.51 mmol) 2,4-dinitrophenylhydrazine in 67 ml 10% perchloric acid solution. After 12 hours at +5°C the resulting yellow precipitate was filtered, washed with water and dried in vacuo to give acetaldehyde dinitrophenylhydrazone, (310 mg, 55%), m.p.: 159°C.

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