

## Cathodic Carbonylation of 1-Halogenopentanes

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Reaction conditions for electroreductive conversion of 1-halogenopentane into hexanal using  $[\text{Fe}(\text{CO})_5]$  have been investigated in detail. The use of acetonitrile as solvent containing tetraalkylammonium halides or toluene-*p*-sulfonate and a divided cell gave good results. Under the conditions, the best results were obtained with the bromide as starting halide.

Since acyl anions are not commonly accessible, nucleophilic acylation is generally achieved with a variety of reagents, among them acylmetallic compounds which are synthetically equivalent to acyl anions.

Organometallic acyl-anion transfer reagents can be produced by the reaction of carbanion donors with carbon monoxide or metal carbonyls. For example, carbon monoxide reacts with organolithium compounds at low temperature to give nucleophilic acylating reagents<sup>1-4</sup> and organolithium compounds<sup>5-10</sup> and Grignard reagents<sup>11-13</sup> react with carbonylnickel or pentacarbonyliron to give acylmetallic compounds; the reaction of organic halides with carbonyl metal anions such as disodium tetracarbonyliron also give such compounds.<sup>14-18</sup> Acylmetallic intermediates are also formed in phase-transfer carbonylation.<sup>19,20</sup>

Electroreduction of alkyl halides gives carbanions by way of radical anions and/or radicals;<sup>21,22</sup> similar reduction of metal carbonyls gave the corresponding anions (e.g. pentacarbonyliron gives tetracarbonyliron dianion).<sup>23,24</sup> In our work we have examined the electroreduction of 1-halogenopentanes with a metal carbonyl, our efforts initially being directed towards finding a suitable solvent-electrolyte system. Here we describe results for a variety of reaction conditions.<sup>25</sup>

### Results and Discussion

In the present work, we selected co-ordinated carbon monoxide as a  $\text{C}_1$  source in the electroreaction (1) where  $\text{RX}$  is 1-bromopentane.



Initially, in a search for optimum reaction conditions, various polar organic solvents containing tetraalkylammonium or alkali metal salts as supporting electrolytes were examined by using a divided cell. Whilst acetonitrile (AN), *N,N*-dimethylformamide (DMF), and *N*-methylpyrrolidinone (NMP) produced good results, dimethyl sulfoxide, hexamethylphosphoric triamide (HMPA), nitromethane and methanol were found to be unsuitable as solvents. Aliphatic quaternary ammonium ions proved useful as supporting-electrolyte cations, whereas alkali metal ions were not. When nonhalide anions such as toluene-*p*-sulfonate ( $\text{OTs}^-$ ) were used as counterions, sparingly soluble compounds formed coatings on the anode surface and led to a progressive increase in the cell voltage. The presence of  $\text{Bu}_4\text{NI}$  in the anodic compartment was effective in avoiding this. Table 1 shows the influence of different electrolyte media on the yields of hexanal brought about by protolytic work-up with aqueous 2 mol  $\text{dm}^{-3}$  HCl. Some 5% of hexanal was recovered from the anolyte after hydrolytic work-up; reported yields take account of these values.

Table 2 summarizes the results carried out with different cell

**Table 1** Cathodic carbonylation of 1-bromopentane<sup>a</sup>

Solvent	Electrolyte	Anodic additive	Conversion (%)	Hexanal yield <sup>c</sup> (%)
AN	$\text{Et}_4\text{NBr}$	None	88	71 (80)
AN	$\text{Et}_4\text{NOTs}$	<i>b</i>	83	68 (83)
AN	$\text{Bu}_4\text{NClO}_4$	<i>b</i>	83	57 (68)
AN	$\text{Bu}_4\text{NBF}_4$	<i>b</i>	86	54 (63)
DMF	$\text{Et}_4\text{NOTs}$	<i>b</i>	92	33 (35)
NMP	$\text{Et}_4\text{NOTs}$	<i>b</i>	69	14 (21)

<sup>a</sup>  $[\text{C}_5\text{H}_{11}\text{Br}] = [\text{Fe}(\text{CO})_5] = 0.1 \text{ mol dm}^{-3}$ ; divided cell; SS cathode; Pt anode; current, 50 mA; electricity, 2.0 F  $\text{mol}^{-1}$ ; proton donor used in work-up, aqueous 2 mol  $\text{dm}^{-3}$  HCl. <sup>b</sup>  $[\text{Bu}_4\text{NI}] = 0.102 \text{ mol dm}^{-3}$ . <sup>c</sup> Based on RBr used. The value in parentheses represents the yield based on RBr consumed.

**Table 2** Influence of cell modes on the yields<sup>a</sup>

Cell	Electrolyte	Conversion (%)	Yield <sup>b</sup> (%)
Divided	$\text{Et}_4\text{NOTs}$	82	67 (82)
Undivided	$\text{Et}_4\text{NOTs}$	37	20 (53)
Divided	$\text{Et}_4\text{NBr}$	88	71 (80)
Undivided	$\text{Et}_4\text{NBr}$	42	23 (54)

<sup>a</sup> Solvent, AN;  $[\text{RBr}] = [\text{Fe}(\text{CO})_5] = 0.1 \text{ mol dm}^{-3}$ ; Pt electrodes; current, 0.05 A; electricity, 2.0 F  $\text{mol}^{-1}$ . <sup>b</sup> Based on RBr used. The value in parentheses represents the yield based on RBr consumed.

**Table 3** Relation between electrical consumption and conversion<sup>a</sup>

EC (F $\text{mol}^{-1}$ )	Conversion (%)	Yield <sup>b</sup> (%)
2.0	83	68 (83)
2.1	86	64 (75)
2.2	>99	63 (63)

<sup>a</sup> Divided cell; solvent, AN; electrolyte,  $\text{Et}_4\text{NOTs}$ ;  $[\text{RBr}] = [\text{Fe}(\text{CO})_5] = 0.1 \text{ mol dm}^{-3}$ ; SS cathode; Pt anode; current, 0.05 A. <sup>b</sup> Based on RBr used. The value in parentheses represents the yield based on RBr unrecovered.

**Table 4** Influence of cathode materials<sup>a</sup>

Cathode	Conversion (%)	Hexanal yield <sup>c</sup> (%)
SS	83	68 (83)
Pt	82	67 (82)
Cu	82	66 (80)
Ni	79	65 (83)
Pb	88	63 (72)
Hg	74	58 (78)
C <sup>b</sup>	76	52 (69)

<sup>a</sup> Divided cell; solvent, AN; electrolyte,  $\text{Et}_4\text{NOTs}$ ;  $[\text{RBr}] = [\text{Fe}(\text{CO})_5] = 0.1 \text{ mol dm}^{-3}$ ; current, 50 mA; electricity, 2.0 F  $\text{mol}^{-1}$ . <sup>b</sup> Vitreous carbon. <sup>c</sup> Based on RBr used. The value in parentheses represents the yield based on RBr consumed.

**Table 5** Effect of changing halide atoms of RX on the nature and yield of products<sup>a</sup>

X of RX	Solvent	Electrolyte	Anodic additive	Conversion (%)	Yield <sup>c</sup> (%)	
					RCHO	R <sub>2</sub> CO
I	AN	Et <sub>4</sub> NOTs	<i>b</i>	96	61	1
I	AN	Bu <sub>4</sub> NI	None	99	58	3
I	NMP	Bu <sub>4</sub> NI	None	>99	40	7
I	NMP	Et <sub>4</sub> NOTs	<i>b</i>	97	22	7
Br	AN	Et <sub>4</sub> NBr	None	88	71	None
Br	AN	Et <sub>4</sub> NOTs	<i>b</i>	83	68	None
Br	NMP	Et <sub>4</sub> NOTs	<i>b</i>	69	14	None
Cl	AN	Et <sub>4</sub> NOTs	<i>b</i>	67	31	None
Cl	AN	Et <sub>4</sub> NCl	None	57	16	None

<sup>a</sup> Divided cell; SS cathode; Pt anode; [RX] = [Fe(CO)<sub>5</sub>] = 0.1 mol dm<sup>-3</sup>; current, 50 mA; electricity, 2.0 F mol<sup>-1</sup>. <sup>b</sup> [Bu<sub>4</sub>NI] = 0.102 mol dm<sup>-3</sup>.

<sup>c</sup> Based on RX used.

types. The use of an undivided cell depressed both yield and percentage conversion.

Table 3 presents the effect of electrical consumption on conversion. Complete consumption of the bromide requires 2.2 F mol<sup>-1</sup> and the data listed show that the yield rather decreased with increasing electrical consumption.

The role of the electrode materials was also examined with different cathodes. As can be seen in Table 4, cathode materials have little effect on the yield of product.

Table 5 presents the effect of changing halide atoms of RX on the nature and yield of products. The data listed in Table 5 show that the order of hexanal yield is RBr > RI > RCl. Alkyl iodide gave a small amount of ketone by-product, a second alkylation during the electroreduction giving the symmetrical compound.

### Conclusions

The best reaction medium for the desired cathodic carbonylation was acetonitrile containing tetraalkylammonium halides (or OTs<sup>-</sup>) in a divided cell. With OTs<sup>-</sup> ion as a counterion, tetraalkylammonium halide must also be used as a depolarizer. Although cathode materials had little effect on the yield of product, use of an undivided cell lowered the percentage conversion. The best results for conversion of 1-halogenopentanes into hexanal were obtained with the bromide.

### Experimental

**Materials.**—Commercial acetonitrile was stirred for 2 days with CaH<sub>2</sub> (10 g dm<sup>-3</sup>) until no further hydrogen was evolved; it was then decanted and fractionally distilled from P<sub>2</sub>O<sub>5</sub> (5 g dm<sup>-3</sup>). This product was refluxed over CaH<sub>2</sub> (5 g dm<sup>-3</sup>) for several hours, slowly fractionally distilled,<sup>26–28</sup> and then stored in a Schlenk tube under a nitrogen atmosphere. *N*-Methylpyrrolidone was, after storage over CaH<sub>2</sub> for a few days, thrice distilled under reduced pressure, stored under a nitrogen atmosphere and used within a few days of the distillation.<sup>29</sup> DMF was dried for 3 days over type 4 Å molecular sieves, during this time several changes of sieves were made, and then fractionally distilled under reduced pressure; nitrogen was passed through the apparatus during the distillation.<sup>26,27</sup>

Et<sub>4</sub>NBr and Et<sub>4</sub>NCl were purchased. The following supporting electrolytes were prepared according to the literature procedure: Et<sub>4</sub>NOTs,<sup>30</sup> Bu<sub>4</sub>NBF<sub>4</sub>,<sup>31</sup> Bu<sub>4</sub>CIO<sub>4</sub>,<sup>31</sup> and Bu<sub>4</sub>NI<sup>32</sup>. 1-Bromo-, 1-chloro-, and 1-iodo-pentane and [Fe(CO)<sub>5</sub>], obtained commercially, were purified by distillation. Hexanal and undecan-6-one as reference materials were commercial samples.

**Electroreduction.**—A standard procedure is illustrated. The reaction was carried out in a divided cell with a stainless steel

(SS) plate cathode (18 cm<sup>2</sup>) and a similar Pt plate anode. The catholyte was composed of acetonitrile (50 cm<sup>3</sup>) 1-bromopentane (5 mmol), [Fe(CO)<sub>5</sub>] (5 mmol), and Et<sub>4</sub>NBr (2.4 g, 11.4 mmol). The anolyte was the same medium in the absence of the substrates. The cathode and anode compartments, kept under a nitrogen atmosphere, were stirred magnetically. The reaction was performed at 50 mA of constant current by using a direct-current power supply at room temperature until 2.0 F mol<sup>-1</sup> of added substrate had passed through the solution, which took ca. 5 h.

After completion of the reduction, the catholyte was treated with aqueous 2 mol dm<sup>-3</sup> HCl and extracted with pentane. The pentane extract was washed with dilute aqueous sodium hydrogencarbonate. The anolyte was similarly treated with aqueous HCl. The extract was washed successively with dilute aqueous sodium thiosulfate and brine. The pentane extract was dried (MgSO<sub>4</sub>), filtered and analyzed by GLC using a PEG 6000 column at 80 °C. GLC analysis showed the presence of hexanal (71% yield based on 1-bromopentane used; 88% yield based on the substrate unrecovered) as the only product, together with a small amount of the unchanged bromide.

When the electroreduction was conducted in an undivided cell, both yield and conversion decreased considerably.

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