Cathodic Alkylation of Methyl Phenylacetate and its η^6-Tricarbonylchromium Complex

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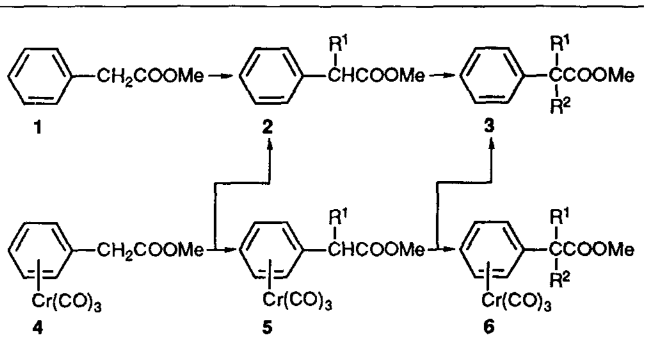
Electrolysis of methyl phenylacetate or its η^6-tricarbonylchromium complex, in MeCN on a Pt cathode in the presence of alkyl bromides, results in mono- and/or di-alkylated products, the yield depending on the nature of the initial reagents. When (methyl phenylacetate)tricarbonylchromium is used decomplexation might also take place as a side reaction.

In developing an electrochemical version of the Perkin-type reactions[1-3] we have previously found that phenylacetic acid esters with low CH-acidity ($pK_a = 23.3$[4]) are reduced with greater difficulty than dihaloalkenes and consequently they are not involved in the named process. This fact does not exclude the possibility of cathodic carbanions generation from phenylacetates,[5,6] *e.g.*, in the presence of $MeSO_2OMe$ the diaphragmic electrolysis of methyl phenylacetate **1** leads to the monomethylated product.[6] Furthermore, we have recently shown[7] that the yield of cathodically-alkylated phenylacetates can be significantly raised by moving to a tricarbonylchromium complex, with the $(CO)_3Cr$-group being readily removed after the process is completed. We connected this fact with the known data for the increase in the benzylic hydrogen atom acidity in the complex **4** compared with the free arene.[8,9]

In this communication we present a study of the electrolysis of methyl phenylacetate **1** and its tricarbonylchromium complex **4** at a Pt cathode in the presence of alkyl bromides, together with a detailed investigation of the product composition for both free arenes **2** and **3** and complexes **5** and **6** (Scheme 1, Table 1). The intermediates in these reactions are obviously the corresponding carbanions $Ar\bar{C}HCOOMe$ [$Ar = C_6H_5$ or $(CO)_3CrC_6H_5$], the interaction of which with RBr results in alkylated compounds **2**, **3**, **5** and **6**. The carbanion formation is due to cathodic cleavage of the benzylic C—H bond in the initial compounds.[5-7]

During the electrolysis of methyl phenylacetate **1** the extent of alkylation was found to be dependent on the quantity of electricity Q passed; the process can be interrupted on monoalkylation. To insert a second methyl, and particularly an ethyl group, is considerably more difficult (Table 1). When 1,3-dibromopropane was used as alkylating agent the ester **1** remained unchanged after electrolysis. In this case C—H bond splitting in ester **1** is in efficient competition with the cathodic reduction of $Br(CH_2)_3Br$ to cyclopropane.[3,10]



2,5	R^1	**3,6**	R^1	R^2
a	Me	**a**	Me	Me
b	Et	**b**	Et	Et
c	$(CH_2)_3Br$	**c**	Me	Et
		d	—$(CH_2)_3$—	

Scheme 1 *Reagents and conditions:* 0.3 mol dm^{-3} Et_4NBr in MeCN, 1–1.25 mmol **1** or **4**, 10 mmol RBr, $j = 1$ mA cm^{-2}, Pt cathode, Mg anode, divided cell, catholyte volume 25 cm^3, anolyte volume 20 cm^3

On transition from **1** to its complex **4** the cathodic dimethyl-

Table 1 Yield of products from the cathodic alkylation of compounds **1**, **4** and **5a**

Initial reagents		Products obtained			
CH-acid	Alkyl bromide	Compound	Analytical yield[a] (%) (Q/F mol^{-1})		
1	MeBr	**2a**	66 (1.0)	97 (1.5)	57 (2.5)
		3a	0 (1.0)	2 (1.5)	43 (2.5)
	EtBr	**2b**	56 (1.0)	95 (2.5)	81 (4.0)
		3b	0 (1.0)	0 (2.5)	19 (4.0)
	$Br(CH_2)_3Br$	—	—		
4	MeBr	**5a**[b]	60 (1.0)	0 (3.0)	48 (1.0)[d]
		6a[b]	10 (1.0)	100 (3.0)	8 (1.0)[d]
	EtBr	**5b**[b]	70 (1.0)	55 (2.0)	3 (5.0)
		6b[c]	0 (1.0)	0 (2.0)	5 (5.0)
		2b	0 (1.0)	45 (2.0)	71 (5.0)
		3b	0 (1.0)	0 (2.0)	21 (5.0)
	$Br(CH_2)_3Br$	**5c**[c]	30 (1.0)	60 (4.0)	0 (7.5)
		6d[b]	0 (1.0)	40 (4.0)	100 (7.5)
5a	MeBr	**6a**[b]	60 (1.0)	100 (2.0)	
	EtBr	**6c**[b]	10 (1.0)	16 (5.0)	
		2a	26 (1.0)	40 (5.0)	
		3c	4 (1.0)	40 (5.0)	

[a] GLC (in the case of complexes the samples were previously subjected to decomplexation by iodine in THF) and ^1H NMR (integral intensities of characteristic signals in the product mixtures). [b] Aromatic *ortho*-proton chemical shifts (C_6D_6, 250 MHz, broad doublets with $J \sim 6$ Hz, δ, ppm): **4**, 4.51; **5a**, 4.91 and 4.56; **5b**, 5.21 and 4.44; **6a**, 5.11; **6b**, 5.42; **6c**, 5.29 and 4.92; **6d**, 4.75. Melting points (°C): **5a**, 37; **5b**, 51; **6a**, 54 (55[9]); **6c**, 64; **6d**, 98.5 (100[9]). [c] The compounds were not individually isolated. [d] Electrolysis of **4** followed by treatment of the catholyte with MeBr.

ation proceeds readily resulting in compound **6a** (Scheme 1). The reaction passes through the monomethyl product **5a** with a low selectivity: at $Q \sim 1$ F mol^{-1} in the catholyte all the three complexes **4**, **5a** and **6a** have been detected (Table 1). When ethyl bromide is used monoalkylation takes place quite easily and at $Q = 1$ F mol^{-1} the complex **5b** was obtained in a 70% yield. Further passage of electricity, however, gives the diethylated complex **6b** only in a small quantity, while the major electrolysis products appear to be the free arenes **2b** and **3b**. Similarly, ethyl bromide does alkylate the monomethylated complex **5a** (Table 1). A comparison of electrolysis results for **5a** in the presence of MeBr and EtBr makes it possible to conclude that the anion $(CO)_3CrC_6H_5\bar{C}(Me)COOMe$ is formed easily, its reaction with MeBr proceeding without complications. On the contrary, less electrophilic and sterically more hindered EtBr should react with such a bulky anion considerably more slowly, consequently the decomplexation process may become preferable, resulting mostly in formation of alkylated free ligands.

The accessibility of alkylated complexes **5** and **6** may be correlated with the chemical shifts of protons at the *ortho*-positions of the arene ligands in their ^1H NMR spectra (Table 1, footnote *b*). In the case of the low-yield compounds **6b, c** compared with the others, the signals of the above-mentioned protons are shifted downfield. This may be connected with the distortion of arene-chromium π-bond symmetry resulting from repulsion of substituents at the α-carbon atom and $Cr(CO)_3$ group.

Insertion of a tricarbonylchromium group into the molecule of methyl phenylacetate **1** makes it possible to achieve not only quantitative but also qualitative changes in the results of the cathodic alkylation. For example, electrolysis of the complex **4** in the presence of $Br(CH_2)_3Br$ leads to the cyclobutane derivative **6d**; as was mentioned above a similar cyclic compound was not formed from arene **1**. It should be noted that electrolysis of complex **4** in the absence of electrophiles ($Q = 1$ F mol^{-1}) followed by treatment of the catholyte with MeBr results in the methylated compounds **5a** and **6a** (Table 1). A similar experiment with the arene **1** fails to give the desired products **2a** and **3a**. This confirms the distinction in stability of the carbanion intermediates $C_6H_5\bar{C}HCOOMe$ and $(CO)_3Cr$-$C_6H_5\bar{C}HCOOMe$.

To conclude, a transition to tricarbonylchromium complexes may allow for an advanced cathodic alkylation of phenylacetic acid esters and related compounds, though this process has appeared to be sensitive to small structural changes in the initial reagents.

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