Electrochemical Acylation of Some Cyclic Olefins by Using Aluminium Anode

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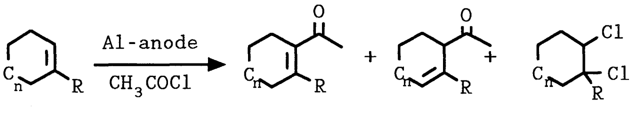
The electrochemical acylation of cyclohexene, cycloheptene and their 1-methyl derivatives produces alkyl-cycloalkenyl ketones in good yields. The unsubstituted cycloalkenes give α,β-unsaturated ketones, whereas the 1-substituted derivatives yield mixtures of α,β- and β,γ-unsaturated ketones in which the latter products are predominant.

Contrary to the well-known Friedel-Crafts acylation of aromatics, the acylation of alkenes by means of acyl halides in the presence of Lewis acids as catalysts was not yet successfully applied in organic synthesis. The main problem arising by running this reaction is the formation of various reactive intermediates as products of electrophilic addition, elimination, and isomerisation, resulting in complex mixtures. Nonetheless, the reaction has been studied,[1-3] since the possible products - unsaturated conjugated and/or nonconjugated ketones - could be of synthetic interest.

In this paper we wish to report that this reaction can be achieved by electrolysis, using an Al-anode and a Cu-cathode immersed in an appropriate medium, containing cycloalkene and an acylating agent. Cyclohexene (**1a**, Scheme 1), cycloheptene (**1b**) and their 1-methyl derivatives (**1c** and **1d**) were used as substrates, but the acylation of cyclohexene was studied in more detail. Thus, electrolysis of a cold 0.2 mol/l solution of tetraethylammonium chloride, containing cycloalkenes **1a** or **1b** and acetyl chloride, in an undivided cell, affords predominantly (up to 80%) the corresponding α,β-unsaturated ketones, i.e. 1-acetylcycloalkenes **2a** and **2b** (see Scheme 1), accompanied by 5-10% of the corresponding 1,2-dichlorocycloalkanes **4a** and **4b**, and variable amounts of unknown products (up to 20%, see Table 1 and Table 2, and the text below). The β,γ-unsaturated ketones **3a** and **3b** were not detected under these reaction conditions.



1a-d 2a-d 3a-d 4a-d

a) n=1, R=H; b) n=1, R=H; c) n=1, R=CH_3; d)n=2 R=CH_3

Scheme 1.

Table 1. Electrochemical Acylation of Cycloalkenes[a]

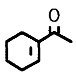
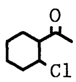
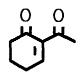
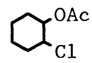
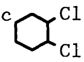
Run	Alkene	Products[b] (Yield)[c]			
		2	3	4	Unknown[d]
1	1a	2a (70-80%)	3a (0 %)	4a (5-7%)	(~ 15%)
2	1b	2b (60-65%)	3b (0%)	4b (5 - 10%)	(~ 20%)
3	1c	2c (10-13%)	3c (75-85%)	4c (1 - 3%)	(traces)
4	1d	2d (20-25%)	3d (65-75%)	4d (1 - 3%)	(traces)

[a] For a typical procedure see the text. [b] Structures were determined on the basis of ^{1}H-NMR, ^{13}C-NMR and IR spectral data. [c] Determined by GLC using an internal standard, and based on the starting alkene. [d] In the case of cyclohexene, some of these products were identified (see Table 2).

However, by using the 1-methyl substituted olefins **1c** and **1d** as substrates, under the same reaction conditions, mixtures of the corresponding α,β- and β,γ-unsaturated ketones (**2c** and **3c** from **1c**, and **2d** and **3d** from **1d**) were obtained, the total yield of ketones being somewhat higher than in the case of the unsubstituted cycloalkenes, but now with a marked predominance of the nonconjugated ketones **3c** and **3d** (Table 1).

A typical procedure is as follows: 30 ml of the 0.2 mol/l solution of $(C_2H_5)_4NCl$ in

Table 2. Electrochemical Acylation of Cyclohexene[a]

Run	Reaction conditions	Yield of products (%)[c]					Unknown
		 2a	 5a	 6a	 7a	 4a	
1	A B C D	60-65	10-19	trace	0-1	1-3	10-13
2	A E C D	55-60	10-15	0-1	trace	2-4	11-15
3	A B F D	65-75	1-5	0-2	0-1	3-10	10-15
4	A B F G	70-80	trace	trace	trace	5-7	7-11
5	H B F D	60-70	1-4	4-7	trace	3-5[d]	10-15
6	H B F G	70-75	trace	trace	trace	5-10[d]	9-13
7	I B F G	70-80	3-5	trace	trace	5-7	7-10
8	I E F G	60-70	5-8	trace	trace	0-1	7-10
9[b]	J	trace	2-5	0-3	25-30	10-15	35-45
10	A B K G	0	0	0	0	75-85	5-10

A: 0.2 mol/l Et_4NCl in CH_2Cl_2, B: AcCl. C: divided cell/Al-anoide. D: 15-18°C. E: Ac_2O. F: undivided cell/Al-anode. G: -10 to -5°C. H: 0.2 mol/l Et_4NBr in CH_2Cl_2. I: 0.1 mol/l Et_4NClO_4 in CH_2Cl_2. J: 0.5 mol/l $FeCl_2$ in Ac_2O/undivided cell/r.t. K: undivided cell//C-anode.

[a]The procedure is described in the text. In the case of electrolysis in the divided cell (a ceramic memrane; 30 ml of the corresponding electrolyte containing the corresponding acylating agent and cyclohexene in the anode compartment; 20 ml of the electrolyte in the cathode compartment) only the anolyte was worked up. [b]10 ml of 0.5 mol/l of $FeCl_2$ containing 5 mmol of cyclohexene was electrolysed at a constant current (100 mA, 1F/mol). After the reaction was completed, the resulting reaction mixture was diluted with 10 ml of water, and neutralised with Na_2CO_3. Further treatment as in previous cases. [c]Determined by GLC and based on the substrate. [d]A mixture of chloro and bromo derivatives of cyclohexane.

dry CH_2Cl_2, containing 5 mmol of the corresponding cycloalkene and 5 mmol of CH_3COCl, was electrolysed at a constant current (200 mA), in an undivided, cooled cell (-10 to -5°C), using aluminium and copper foils in the form of a cylinder as an anode and cathode respectivelly. After reaction was completed (3 F/mol), the solvent was evaporated in vacuo, the residue extracted with n-hexane, washed successively with saturated solutions of Na_2CO_3 and NaCl and water, and finally dried over anhydrous Na_2SO_4. The residue obtained after evaporation of the solvent was analysed and separated by analytical and preparative GLC.

Generally, conjugated enones are thermodynamically more stable than their β,γ-isomers, although exceptions are known.[4] This fact explains the formation of compounds **2a** and **2b** by the acylation of unsubstituted olefins **1a** and **1b**, and suggests a thermodynamically controlled reaction. However, the ratio of the products of acylation of cycloalkenes **1c** and **1d** probably does not manifest their stability ratio, although the trisubstituted double bond is relatively reluctant to shift into conjugation with the carbonyl group.[5]

The reaction was studied in more detail in the case of cyclohexene. In Table 2 are summarised the results obtained by varying the reaction conditions. As can be seen, a good yield of ketone **2a** can be achieved by electrolysis using an aluminium anode in a chloride, bromide, and perchlorate medium. Acetic anhydride can also be used as an acylating agent. The electrolysis in a divided cell gives an almost same yield of **2a**, but some amounts of 1-acetyl-2-chlorocyclohexane (**5a**), 2-acetylcyclohex-2-en-1-one (**6a**), and 2-chlorocyclohexyl acetate (**7a**) are formed too. Lower temperatures provide a little higher yield of ketone **2a** and a cleaner reaction.

The electrolysis of a solution of cyclohexene and acetyl chloride in a chloride medium using graphite as an anode does not give ketone, but almost pure 1,2-dichlorocyclohexane (**4a**).

Attempts to obtain 1-acetylcyclohexene by electrolysis of an acetic anhydride solution of cyclohexene and $FeCl_2$, using a graphite anode, failed (see Table 2, run 9).

References and Notes

1 H. M. Hoffmann and T. Tsushima, *J. Am. Chem. Soc.*, **99**, 6008 (1977).

2 M. Santelli, A. Tubul, and C. Morel-Fourier, NATO ASI Ser., Ser. C **1989**, 289, 127.

3 F. X. Bates, J. A. Donnelly, and R. Keegan, *Tetrahedron*, **47**, 4991 (1991).

4 N. Heap and G. H. Whitham, *J. Chem. Soc., B*, **1966**, 164.

5 N. C. Deno and H. Chafetz, *J. Am. Soc.*, **74**, 3940 (1970).