Use of a Sacrificial Aluminum Anode in the Acylation of Some Olefins

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The acylation of some alicyclic and aliphatic alkenes by the electrochemical generation of a catalyst using a sacrificial aluminum anode was investigated. Substrates were electrolyzed in a dichloromethane solution of an appropriate electrolyte (tetraalkylammonium salts) in the presence of an acylating agent (acetyl chloride or anhydride). Thus, unsubstituted cycloalkenes, namely cyclohexene and cycloheptene, gave by that reaction conjugated ketones, i.e. the corresponding 1-acetylcycloalkenes, as the only unsaturated carbonyl compounds in moderate-to-good yields. Under the same reaction conditions their 1-methyl derivatives gave mixtures of the corresponding conjugated and β,γ-unsaturated isomeric ketones in which unconjugated compounds predominate. In both cases unsaturated ketones were accompanied by different amounts of side products. Terminal aliphatic alkenes (1-hexene, 1-heptene, and 1-dodecene) afforded only conjugated a ketone with a normal skeleton, but in lower yields. The acylation of cyclohexene was studied in more detail, altering the reaction conditions by changing the reaction temperature, the supporting electrolyte, the acylating agent and the electrochemical cell. Mechanistic considerations were made on the basis of the products distribution and some theoretical calculations being made by the MOPAC program package (version 7.0).

The reactions of olefins, functionalized or not, with electrophilic reagents are a powerful tool for organic synthesis, and have been studied in many laboratories. In our laboratories we also investigated such types of transformations, and many reactions of unsaturated alcohols and acids with the electrophiles, such as salts of lead(IV) and tallium(III), and electrochemically generated phenylselenenyl ions are utilized for the synthesis of β-functionalized cyclic ethers and lactones.[1] In a continuation of these investigations, we have been interested in the famous interaction of unfunctionalized olefins with an acyl cation (produced from carboxylic acid halides or anhydrides and Lewis acids), expecting unsaturated ketones as the products.

Although this reaction (known as the Friedel–Crafts aliphatic acylation) has been widely studied since the end of the last century,[2] it was not yet satisfactorily applied in organic synthesis, contrary to the analogous acylation of aromatics, discovered only about fifteen years earlier (1877). The problems arising by running acylation of olefins are the consequence of the formation of reactive intermediates which undergo different transformations by processes such as additions, eliminations and isomerizations, resulting in a complex mixture of products whose separation is very difficult. Nonetheless, the validity of the possible reaction products (conjugated and/or nonconjugated unsaturated ketones) for the organic synthesis, and the relatively cheap substrates were a driving force for numerous research projects to be concerned with that problem. Many articles describing the acylation of alkenes by using different Lewis acids as catalysts (salts of Al(III), Zn(II), Sn(IV), and Sb(V), alkylaluminum compounds etc.) have appeared in the literature, even almost 100 years after its discovery.[3]

On the other hand, the electrochemical generation of any catalyst for the acylation of alkenes with anodic dissolving metals has not yet been reported in the literature, although the use of a sacrificial anode can be one possible way to introduce metal cations into the reaction medium. We can avoid many operational problems, such as purification, sublimation, air and moisture protection, dosage complications etc, encountered when we use commercially available reagents. Recently, Gambino et al.[4] reported that aluminum-based catalysts can be generated by the anodic dissolution of the metal in a solution of aluminum(III) chloride and acetyl chloride in benzene, resulting in acylation of the solvent. However, the yield of acetophenone (which is accompanied with 1,2-diphenyl-ethane) in this reaction, calculated on the basis of either the most expensive reagent (acetyl chloride), or benzene (as organic chemists usually do) was very poor.

Recently, we reported that the electrochemical generation of catalysts by using sacrificial aluminum anode can be a potentially useful method for the acylation of cycloalkenes.[5] In the present paper we wish to report on our complete results, including experimental details, spectral data of the obtained products, and mechanistic considerations supported by some

theoretical calculations derived by using the MOPAC program package (version 7.0).

Results and Discussion

The present investigations were started with acylation of cyclohexene (**1a**), cycloheptene (**1b**), 1-methylcyclohexene (**1c**), and 1-methylcycloheptene (**1d**) by the electrolysis of a cold dichloromethane solution of these substrates in the presence of acetyl chloride as an acylating agent. The reaction was carried out in an undivided cell supplied with an Al-anode and a Cu-cathode, using tetraethylammonium chloride as an electrolyte. Two unsubstituted cycloalkenes, **1a** and **1b**, gave the corresponding unsaturated conjugated ketones, i.e. 1-acetylcyclohexene (**2a**) and 1-acetylcycloheptene (**2b**), in moderate-to-good yield (60—80%). The corresponding β,γ-isomers, such as nonconjugated ketones 3-acetylcyclohexene (**3a**) and 3-acetylcycloheptene (**3b**), were not detected among the reaction products. On the other hand, 1-methyl substituted cycloalkenes, **1c** and **1d**, underwent acylation to give mixtures of conjugated and nonconjugated enones (1-acetyl-2-methylcyclohexene **2c** and 3-acetyl-2-methylcyclohexene **3c**, i.e. 1-acetyl-2-methylcycloheptene **2d** and 3-acetyl-2-methylcycloheptene **3d**), in which β,γ-isomers predominated. However, the total yield of the ketones was somewhat higher than in the case of the unsubstituted cycloalkenes (up to 95%). As can be seen from data listed in Table 1, the ratio of two isomers was **2c/3c** = 10 : 90 to
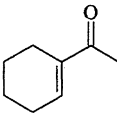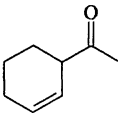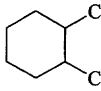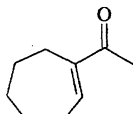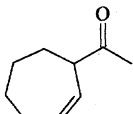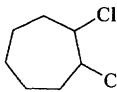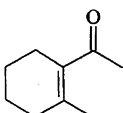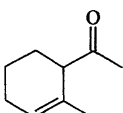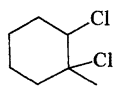
15 : 85, i.e. **2d/3d** = 21 : 79 to 26 : 74.

In all acylation reactions the produced reaction mixtures, besides ketones, contained the corresponding 1,2-dichlorocycloalkanes, namely 1,2-dichlorocyclohexane (**4a**), 1,2-dichlorocycloheptane (**4b**), 1,2-dichloro-1-methylcyclohexane (**4c**), and 1,2-dichloro-1-methylcycloheptane (**4d**) (1—10%), and variable amounts of unknown products (up to 20%). However, the acylation of 1-methylcycloalkenes is a "cleaner" reaction, i.e. only 1—3% impurities being products of side reactions accompanying two isomeric ketones.

With the aim of establishing the best conditions for the acylation of alkenes by electrochemical generation of the catalyst, the acylation of cyclohexene was studied in more detail with respect to the reaction temperature, supported electrolyte, acylating agent, and electrochemical cell. Besides ketone **2a** and dichloro derivative **4a**, another three side products of electrochemical acylation were isolated and identified as 2-acetyl-2-cyclohexen-1-one (**5**), 1-acetyl-2-chlorocyclohexane (**6**), 2-chlorocyclohexyl acetate (**7**). These results are given in Scheme 1 and Table 2, and can be summarized as follows.

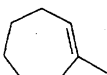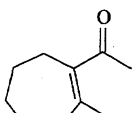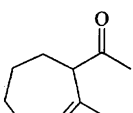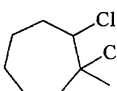Comparing the results in Runs 1, 3, and 5 of Table 2 with the results in Runs 2, 4, and 6, respectively, it can be seen that a lower reaction temperature allows some better yield of conjugated ketone **2a**. The data listed in Table 2 also show that the use of tetraethylammonium chloride or perchlorate as an electrolyte gives better yields of the mentioned compound in

Table 1.   Electrochemical Acylation of Cycloalkenes[a]

Run	Substrate	Products and yields (%)[b]					
1	**1a**	**2a** 70—80	**3a** 0	**4a** 5—7			Unknown (ca. 11)
2	**1b**	**2b** 60—65	**3b** 0	**4b** 5—10			(ca. 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) Reactions were carried out at -10 to -5 °C, by using acetyl chloride as an acylating agent in an undivided cell (see General Procedure for the electrolysis).   b) Structures were determined by IR, ^{1}H NMR, and ^{13}C NMR spectral data; Yields based on starting substrates were determined by GC.

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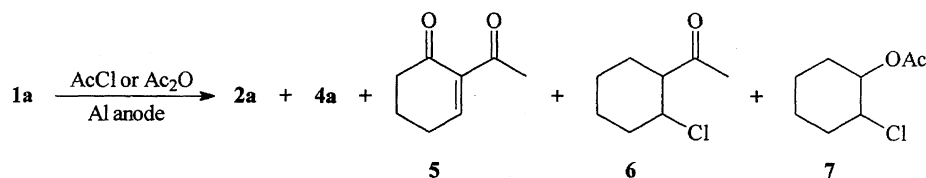
Scheme 1. Electrochemical acylation of cyclohexene.

Table 2. Electrochemical Acylation of Cyclohexene by Using Aluminum Anode

| Run | Reaction conditions | | | | Yield of products (%)[a] | | | | | |
	Temperature °C	Acylating agent	Supported electrolyte mol dm^{-3}	Cell	2a	4a	5	6	7	Unknown
1	15 to 18	AcCl	0.2 Et$_4$NCl/CH$_2$Cl$_2$	Undivided	65—75	3—10	0—2	1—5	0—1	10—15
2	−10 to −5	AcCl	0.2 Et$_4$NCl/CH$_2$Cl$_2$	Undivided	70—80	5—7	T[b]	T[b]	T[b]	7—11
3	15 to 18	Ac$_2$O	0.2 Et$_4$NCl/CH$_2$Cl$_2$	Undivided	60—70	3—5	T[b]	2—4	1—4	10—14
4	−10 to −5	Ac$_2$O	0.2 Et$_4$NCl/CH$_2$Cl$_2$	Undivided	65—75	3—5	T[b]	T[b]	1—2	8—12
5	15 to 18	AcCl	0.2 Et$_4$NBr/CH$_2$Cl$_2$	Undivided	60—70	3—5[c]	4—7	1—4	T[b]	10—15
6	−10 to −5	AcCl	0.2 Et$_4$NBr/CH$_2$Cl$_2$	Undivided	70—75	5—10[c]	T[b]	T[b]	T[b]	9—13
7	−10 to −5	Ac$_2$O	0.2 Et$_4$NBr/CH$_2$Cl$_2$	Undivided	60—65	4—6[c]	T[b]	2—4	T[b]	7—13
8	−10 to −5	AcCl	0.1 Et$_4$NClO$_4$/CH$_2$Cl$_2$	Undivided	70—80	5—7	T[b]	3—5	T[b]	7—10
9	−10 to −5	Ac$_2$O	0.1 Et$_4$NClO$_4$/CH$_2$Cl$_2$	Undivided	60—70	0—1	T[b]	5—8	T[b]	7—10
10	15 to 18	AcCl	0.2 Et$_4$NCl/CH$_2$Cl$_2$	Divided	60—65	1—3	T[b]	10—19	0—1	10—13
11	15 to 18	Ac$_2$O	0.2 Et$_4$NCl/CH$_2$Cl$_2$	Divided	55—60	2—4	0—1	10—15	T[b]	11—15

a) Yields based on the starting substrate determined by GC.   b) Trace amounts.   c) A mixture of chloro and bromo derivatives of cyclohexane.

comparison with the reactions in which the reaction conditions are the same, except for the use of tetraethylammonium bromide as the electrolyte (compare the results in Runs 1, 2, 4, and 8 with those in Runs 5, 6, and 9, respectively).

The effect of an acylating agent on the production of ketone 2a by the present techniques can not be ruled out; slightly better results were obtained when acetyl chloride was used instead of acetic anhydride (compare the Runs 1, 2, 6, and 8 with 3, 4, 7, and 9, respectively).

As can be seen from data in Table 2, the electrolysis of cyclohexene in an appropriate medium using a divided cell with an Al anode gives a somewhat lower yield of ketone 2a, but a marked higher yield of saturated ketone 6.

Unknown products of the present reaction are viscous oils, whose IR and NMR spectra point to chemical structures which include carbonyl and acyloxy groups, olefinic bonds, and atoms of halogens.

In order to make sure that acylation of olefins proceeds by the aid of the generation of an Al species under the conditions

as the electrolysis proceeds, hexene has been electrolyzed in a dichloromethane/tetraethylammonium chloride system in the presence of acetyl chloride, but with a graphite or platinum anode. No acylation products were found in those cases, but 1,2-dichlorocyclohexane has been isolated as the sole product in 75—80% yield (see Table 3).

The acylation of cyclohexene was also studied as a process catalyzed by iron salts; the results are listed in Table 3 (Runs 2, 3, and 4). As can be seen, attempts to obtain 1-acetyl-cyclohexene in an acetic anhydride/iron(II) chloride system using graphite or platinum as an anode failed. Under these conditions the acylating products were derived only in 2—8% yields together with trace amounts of enone 2a. On the other hand, electrolysis of cyclohexene in a dichloromethane solution of tetraethylammonium chloride or bromide using an Fe-anode afforded acylation of the substrate, though the yield of ketone 2a was significantly lower than by using the aluminum one. Also, in those cases the amount of unknown products was considerably higher. Contrary to the acylation
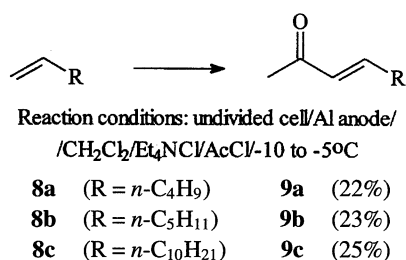
Table 3.   Electrolysis of Cyclohexene in an Undivided Cell by Using C, Pt and Fe Anode

Run	Reaction conditions				Yield of products (%)[a]					
	Temperature °C	Acylating agent	Supported electrolyte mol dm⁻³	Anode	2a	4a	5	6	7	Unknown
1	15 to 18	AcCl	0.2 Et_4NCl/CH_2Cl_2	C or Pt	—	75—85	—	—	—	—
2	−10 to −5	Ac_2O	0.5 $FeCl_2/Ac_2O$	C or Pt	T[b]	10—15	0—3	2—5	25—30	35—45
3	15 to 18	AcCl	0.2 Et_4NCl/CH_2Cl_2	Fe	20—27	9—12	T[b]	8—9	2—3	40—50
4	−10 to −5	AcCl	0.2 Et_4NBr/CH_2Cl_2	Fe	53—58	3—5	T[b]	7—9	T[b]	20—30

a) Yields based on the starting alkene determined by GC.   b) Trace amounts.

of the same substrate by using aluminum as an anode, the yield of enone **2a** was higher when tetraethylammonium bromide was used as an electrolyte.

The present reaction has also been applied to the acylation of aliphatic olefins. 1-Hexene (**8a**), 1-heptene (**8b**), and 1-dodecene (**8c**) were chosen as the substrates; it was observed that since the reaction obeyed the Markovnikov rule, only conjugated 2-oxo derivatives with normal skeleton were obtained. However, acylation of these alkenes gave lower yields of the corresponding ketones than did the acylation of cycloalkenes. Thus, conjugated ketones 3-octen-2-one (**9a**), 3-nonen-2-one (**9b**), and 3-tetradecen-2-one (**9c**) were derived in only 22—25% yield, calculated on the basis of the corresponding starting alkenes (determined by GC), as can be seen in Scheme 2. It should be noted that better yields of acylation products can be achieved by performing a reaction in which alkene is present in significant excess. Thus, the best conditions for the acylation of alkene **8c** by the present technique involve 0.5 molar equivalent of acetyl chloride as an acylating agent and 0.75 F mol⁻¹ of electricity. In that case, ketone **9c** was obtained in the 25% yield (GC; calculated on the basis of starting alkene). However, separation by the column chromatography (SiO_2; petroleum ether then petroleum ether/ethyl acetate 9 : 1) gave 54% of unchanged olefin, 22% of enone **9c**, and 20% of mixture of unknown products, so that the isolated yield of **9c** calculated on the basis of substrate consumed was 48%, i.e. 44% on the basis of acetyl chloride.

Reaction conditions: undivided cell/Al anode/
/CH_2Cl_2/Et_4NCl/AcCl/-10 to -5°C

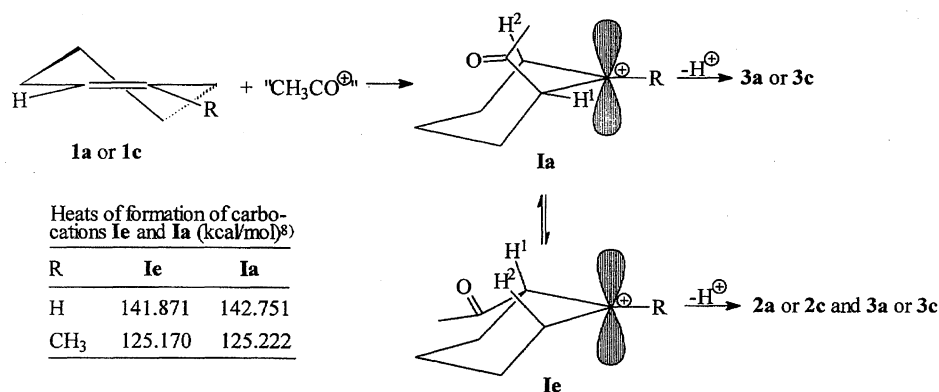|			
8a	(R = n-C_4H_9)	**9a**	(22%)
8b	(R = n-C_5H_{11})	**9b**	(23%)
8c	(R = n-$C_{10}H_{21}$)	**9c**	(25%)

Scheme 2.   Electrochemical acylation of aliphatic alkenes (yields based on the starting substrates determined by GC).

It should also be noted that the quantity of unknown products yielded by the acylation of aliphatic olefins is increased by a prolonged electrolysis time as well as by increasing the acetyl chloride/alkene ratio.

It is not easy to explain the obtained results, especially the different behavior between the unsubstituted and substituted cycloalkenes under the same reaction conditions. Although the conjugated ketones are thermodynamically more stable than their β,γ-isomers,[6] the absence of the latter compounds among the acylation products of alkenes **1a** and **1b** is a surprise. If we accept that the thermodynamic stability difference is the predominant cause for such a distribution of the products in the case of the acylation of unsubstituted cycloalkenes, the results obtained from the acylation of 1-alkylated cycloalkenes should have exhibited the same trend, even if we assume that a trisubstituted double bond is relatively reluctant to shift into conjugation with the carbonyl group.[7] In other words, the ratio of conjugated and nonconjugated ketones does not manifest the ratio of their stability and, therefore, the reasonable explanation for this trend should be made, for instance, by mechanistic considerations.

We suppose that the reaction might be initiated by an electrophilic attack of the acyl cation (produced from an acylating agent and some kind of aluminum species generated from the anode) to the double bond, resulting in an α-acetyl carbocation in which the acetyl group can occupy an axial or equatorial position, as illustrated in Scheme 3 (**Ia**, R=H or CH₃ i.e. **Ie**, R=H or CH₃). Although the cations **Ie**, which can be the precursors for both conjugated (**2**) and unconjugated ketones (**3**), are more stable than the cations **Ia**, which can be the precursor for only unconjugated ketones **3** (see Scheme 3), the energies of the transition states for the formation of the cations **Ie** (153.654 kcal mol⁻¹ for R=H and 142.940 kcal mol⁻¹ for R=CH₃, calculated by using of the MOPAC)[8] are higher than energies of transition states for the formation of the cations **Ia** (152.102 kcal mol⁻¹ for R=H and 140.223 kcal mol⁻¹ for R=CH₃).[8] On the basis of these findings, it would be expected that the formation of **Ia**, rather than **Ie**, might predominate at the initial stage of the reaction. Since the conformational conversion from **Ia** to **Ie** should suffer from a torsional strain between the group R and

Heats of formation of carbo- cations Ie and Ia (kcal/mol)[8]		
R	Ie	Ia
H	141.871	142.751
CH₃	125.170	125.222

Scheme 3.   Formation of 2-acetylcyclohexyl (R=H) and 2-acetyl-1-methylcyclohexyl cations (R=CH₃) and production of the corresponding ketones.

the acetyl group, this process is easier in the case of alkene **1a** (R=H) than in the case of **1c** (R=CH₃). If this is the case, the deprotonation of α-acetyl carbocation generated in the acylation of alkene **1a** takes place after its conversion to the **Ie**-type intermediate, giving a conjugated ketone as the more stable isomer. In the case of **1c**, however, the cation with the axial acetyl group lives longer enough to provide an enhanced chance to be deprotoneted in **Ia**, giving a β,γ-unsaturated ketone as the main product.

Another theoretical consideration can also be of benefit for explaining the obtained results. An analysis of the bonds energy with respect to the C–H bond to be cleaved in carbocations **Ie** and **Ia** (designed as H¹ and H² in Scheme 3) should be informative in this context. For instance, the bond energy of C–H¹ or C–H² in the cation formed from cyclohexene (**Ie**, R=H) is −11.2072 or −11.2762 eV, respectively,[8] which means that deprotonation leading to the conjugated ketone is more favorable than that leading to the β,γ-isomer. On the other hand, according to the bond energy of C–H¹ (−11.4801 eV) or C–H² (−11.4738 eV) in the cation derived from 1-methylcyclohexene (**Ie**, R=CH₃),[8] a rather easier formation of an unconjugated than a conjugated ketone can be expected. If we accept that the 1-methyl-2-acetylcyclohexyl cation partially loses the proton before the conversion of **Ia** to **Ie**, the preferred formation of ketone **3c** can be understood.

The ketone **6** can be formed through a nucleophilic attack of a chloride ion on the cation derived from the first step of the reaction (**Ia** or **Ie**, R=H). It is possible that some amounts of this compound undergo an elimination of HCl during a prolonged reaction time or during a work up, giving the corresponding unsaturated ketone. However, a mechanism by which we can explain the formation of dichlorides **4** and chloro acetate **7** is unclear. Although these compounds might be formed by the addition of chlorine to olefin via 1-chloro carbocation, it is not clear how the chloride ion can be oxidized to chlorine on a sacrificial anode.

As can be seen by comparing the results presented here to those obtained by conventional methods, the present technique is a suitable method for the acylation of alkenes. The yields of the corresponding ketones are comparable with those reported in the literature.[3] For example, Shono et al.[3] reported that the acylation of cyclohexene at 0—5 °C, cat-alyzed by AlCl₃, affords ketone **2a** in only 50% yield. The same authors also reported that better yields of aliphatic and cycloalkenyl-alkyl ketones can be achieved by acylation of the corresponding olefins, but that the use of a sensitive catalyst, active zinc, is necessary.

Experimental

Materials.   All of the chemicals, substrates, and electrode materials used were commercially available. Dichloromethane was dried over P₂O₅ and distilled. The other chemicals were used as received.

Instrumentation.   GC analyses were carried out with a Perkin–Elmer instrument Model 3920B, consisting of a FID detector, 2 m long metal columns of 2 mm diameter packed with 5% Carbowax 20M adsorbed on Chromosorb P; argon was used as a carrier gas. In quantitative analyses acetophenone was served as an internal standard. Preparative GC were made by a Varian-Aerograph chromatograph (Model 920) provided with 2 m long metal columns of 5 mm diameter, fitted with 10% Carbowax 20M adsorbed on Chromosorb P, by using hydrogen as a carrier gas. IR measurements were carried out with a Perkin–Elmer instrument (Model 137B). NMR spectra were obtained with a Varian Gemini (Model 200) spectrometer (200 MHz) by using TMS as a standard and deuteriochloroform as a solvent. As a direct-current source, a Uniwatt, Beha Labor–Netzgerat (NG 394), was used.

Electrochemical Cells.   A cylindrical glass vessel, supplied with a magnetic stirrer, an aluminum anode and a copper cathode (foils in the form of concentric cylinders; each electrode was 5 cm long; diameters of the anode and the cathode were 2.5 and 1.5 cm, respectively) was used as an undivided cell for acylation reactions. As a divided cell the same vessel was used, but the electrodes were separated by a ceramic membrane.

Platinum and iron electrodes used were vaving the same dimensions as the aluminum one, although the graphite electrode was 1 cm diameter and 5 cm long.

General Procedure for the Electrolysis.   For the acylation of alkenes in an undivided cell, placed in the corresponding bath (water at 15—18 °C or an acetone/ice/salt combination), a solution of the supporting electrolyte [0.2 mol dm⁻³ (C₂H₅)₄NCl or (C₂H₅)₄NBr; 0.1 mol dm⁻³ (C₂H₅)₄NClO₄] in dry dichloromethane (30 ml), containing 5 mmol of the corresponding alkene and 5 mmol of an acylating agent [CH₃COCl or (CH₃CO)₂O], was electrolyzed at a constant current (200 mA). After the reaction was completed (3 F mol⁻¹), the solvent was evaporated in vacuo, the residue carefully extracted with three 20 ml portions of hexane,

washed successively with saturated solutions of $NaHCO_3$ and NaCl and·water, and finally dried over anhydrous Na_2SO_4. The residue obtained after the solvent had been distilled off was analyzed and separated by analytical and preparative GC. Only in the case of 1-dodecene (**8c**) was the residue obtained separated by column chromatography (SiO_2, petroleum ether then petroleum ether/ethyl acetate 9 : 1). If electrolysis was made in acetic anhydride as a solvent, the reaction mixture was first hydrolyzed, neutralized by saturated $NaHCO_3$, extracted with hexane and then worked up as in the previous case.

By electrolysis in a divided cell, the anode and cathode compartments were filed with the solution of the supporting electrolyte (30 and 20 ml, respectively), and the corresponding alkene and acylating agent were placed in the anode compartment. After the reaction was completed (constant current of 100 mA; 3 F mol^{-1}), only the anolyte was worked up, as described for electrolysis in the undivided cell.

Spectral Data of Compounds Isolated: 1-Acetylcyclohexene (**2a**),[9] 1-acetyl-2-methylcyclohexene (**2c**),[10] 3-acetyl-2-methylcyclohexene (**3c**),[10] 3-acetyl-2-methylcycloheptene (**3d**),[10] 1,2-dichlorocyclohexane (**4a**),[9] 1-methyl-1,2-dichlorocyclohexane (**4c**),[11] 2-acetyl-2-cyclohexen-1-one (**5**),[12] 1-acetyl-2-chlorocyclohexane (**6**),[14] 2-chlorocyclohexyl acetate (**7**),[13] 3-octen-2-one (**9a**),[11] and 3-nonen-2-one (**9**)[15] are known compounds.

1-Acetylcycloheptene (2b): IR 1660 cm^{-1} (C=O); ^{1}H NMR (CDCl₃) δ=7.10 (1H, m), 2.28 (3H, s), 2.22—2.58 (4H, m), 1.40—1.95 (6H, m); ^{13}C NMR (CDCl₃) δ=199.0, 156.4, 145.4, 26.6, 25.6, 25.2, 25.6, 25.9, 28.7, 31.8.

1-Acetyl-2-methylcycloheptene (2d): IR 1640 cm^{-1} (C=O); ^{1}H NMR (CDCl₃) δ=1.84 (3H, m), 2.21 (3H, m), 1.94—2.39 (4H, m), 1.42—1.81 (8H, m); ^{13}C NMR (CDCl₃) δ=205.2, 154.8, 139.6, 36.9, 32.3, 22.9, 29.6, 29.4, 25.1, 26.7.

1,2-Dichlorocycloheptane (4b): IR 750 cm^{-1} (C-Cl); ^{1}H NMR (CDCl₃) δ=1.45—2.09 (6H, m), 2.10—2.30 (4H, m), 4.25 (2H, m); ^{13}C NMR (CDCl₃) δ=67.2 (2C), 33.2, 26.8 (2C), 22.4 (2C).

3-Tetradecen-2-one (9c): IR 1675 cm^{-1} (C=O); ^{1}H NMR (CDCl₃) δ=0.94 (3H, m, *J*=), 1.10 (14H, m), 1.48 (2H, m), 2.11 (2H, m), 2.15 (3H, s), 6.09 (1H, m, *J*=), 6.78 (1H, m).

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