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The Effect of Electrochemically Formed Aluminum Salts on The Electrochemical Cyclisation of Methyl Cinnamate

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Abstract : Electrochemical cyclisation of methyl cinnamate with dielectrophiles has been improved by the presence of an aluminum salt which was pre-formed *in situ* by the electrolysis of a carboxylic acid with a sacrificial aluminum anode. High yields of three, five and six-membered cyclic products have been obtained in the reactions of methyl cinnamate with dichloromethane, 1,3-dibromopropane, and 1,4-dibromobutane.

Keywords: Electrochemical reactions, cyclisation, sacrificial anode

Electrochemical cyclisation reactions of activated alkenes produce interesting three, five, and six membered cycloalkanes which are synthetically important intermediates. A limited number of these alkenes give good yields of cyclic products,[1-3] for example, cinnamate esters are known to form 2,3-diphenyl-5-oxo-cyclopentanecarboxylates exclusively by electrochemical hydrodimerisation.[1a]

Ring formation through intermolecular coupling of alkenes with dielectrophiles under electrochemical conditions have also been described.[4-6] Improved yields of cyclopropane and cyclopentane derivatives were observed in the presence of electrochemically formed metal ions by using a sacrificial anode in an undivided cell.[5] Although a wide selection of alkenes and dihalides produced corresponding cyclic derivatives, due to low product yields the method is still far from synthetic utilisation. It was suggested that in the course of the reduction process, simultaneous release of metal cations from a sacrifical anode under electrolytic conditions, especially aluminum ions, promoted the cyclisation reactions of activated alkenes with dielectrophiles. However, rapid consumption of alkenes has been observed in the early stages of the electrolyses, whereas metal cations were low in concentration. Consequently, almost half of the substrate did not react in the cyclisation stage due to the absence of sufficient amount of available aluminum ions in the system.

We studied the coupling of activated alkenes with dielectrophiles under sacrifical anode conditions in order to improve the desired product yields. In a new approach, an organic acid was converted into its aluminum salt electrochemically by using a sacrifical aluminum anode in an undivided cell, just prior to the electrolysis of methyl cinnamate with a dielectrophile. The presence of a pre-formed aluminum salt has increased the yields of the cyclisation products as expected.

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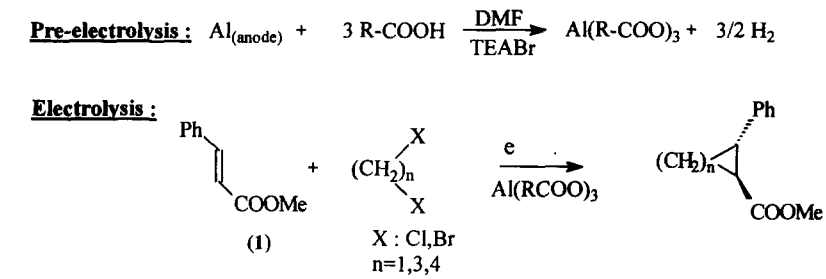
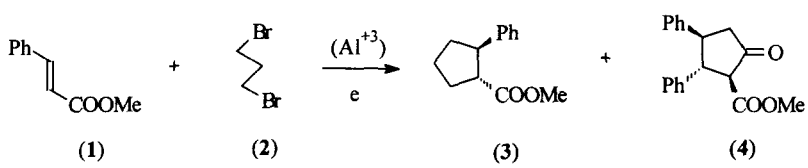


Optimum conditions for high cinnamate conversions and cyclic product yields have been obtained in a set of electrolyses by controlling the amount and the type of the organic acid, and also the type of the solvent-electrolyte system. The electrolysis results of methyl cinnamate (**1**, 0.2M) with 1,3-dibromopropane (**2**, 0.4M) in the presence of an Al salt of different organic acids, is given in Table 1. These reactions have been carried out at constant current (current density 1-2A/dm^2) in different solvent-electrolyte solutions using a sacrifical aluminum anode and a stainless steel cathode in an undivided cell. Before each electrolysis a specified amount of an organic acid was first electrolysed under vigorous passage of N_2. During this period of electrolysis, evolution of hydrogen gas at the cathode and dissolution of the Al anode have been observed. After 1.2-1.5F/mol charge consumption, the cell current went down to the background level which indicated the formation of the aluminum-acid salt. Its formation was proved in a separate electrolysis; where aluminum benzoate was formed in an undivided cell electrochemically, isolated and structurally identified. Following the electrochemical *in situ* preparation of the aluminum-acid salt, methyl cinnamate (**1**) and 1,3-dibromopropane (**2**) were added and electrolysed until 3-4 F/mol electricity were consumed. The isolated main product of each reaction is given in the table.



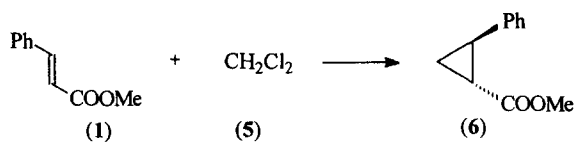
Stronger acids ($pK_a \leq 3$) are sufficient enough to provide the required conductivity, but after the formation of the acid-aluminum salt, they inexplicably caused an electrode passivation, hence electrolyses could not be carried out until completion. On the other hand weaker carboxylic acids, acetic and benzoic acids gave better results. Both cyclic products (**3** and **4**) of methyl cinnamate have been isolated and identified by comparing the spectral results with literature data.[5,7] The *trans*-stereoisomer of methyl 2-phenylcyclopentanecarboxylate was found to be dominant and no *cis*-product could be isolated.[8] As seen in Table 1, DMF/TEABr (*N,N*-dimethylformamide/tetraethylammonium bromide) was observed to be the better solvent-electrolyte sytem for the method. The course of the reaction changed when the supporting electrolyte, TEABr, was replaced with $LiClO_4$; only the cyclic hydrodimer was observed as the major product.

Table 1- The effect of pre-formed aluminum salts of different organic acids on the electrochemical cyclisation of methyl cinnamate (1) with 1,3-dibromopropane (2).

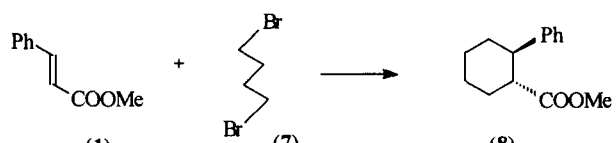
Entry	Organic Acid (M)	Solvent / Electrolyte	Major Product	Yield[1] (%)
1	p-Tos-OH (0.1)	DMF/TEABr	-[2]	-
2	p-Tos-OH (0.1)	DMF/ -[3]	-[2]	-
3	Trifluoroacetic acid (0.1)	DMF/ -[3]	-[2]	-
4	Trichloroacetic acid (0.1)	DMF/ -[3]	-[2]	-
5	Benzoic acid (0.1)	DMF/TEABr[4]	**3**	55
6	Benzoic acid (0.05)	DMF/TEABr[4]	**3**	60
7	Benzoic acid (0.02)	DMF/TEABr[4]	**3**	75
8	Benzoic acid (0.02)	NMP/TBAI/$TBABF_4$	-	-
9	Acetic acid (0.1)	DMF/TEABr[4]	**3**	78
10	Acetic acid (0.05)	DMF/TEABr[4]	**3**	65
11	- -	DMF/TEABr	**3**	50
12	- -	NMP/TBAI/$TBABF_4$	**3**	20
13	- -	DMF/$LiClO_4$	**4**	70

1) Isolated product yields relative to cinnamate used; 2) Reactions did not continue to completion due to electrode passivation, 3) No supporting electrolyte used. 4) 0.05M.

The cyclisation reactions of methyl cinnamate (**1**) with dichloromethane (**5**) and 1,4-dibromobutane (**7**) have been carried out under optimised electrolysis conditions (unless otherwise indicated; undivided cell, Al anode, stainless steel cathode, DMF/TEABr, 0.02M benzoic acid or 0.1M acetic acid, constant current,1-2A/dm^2, 3-4F/mol).



(**1**) (**5**) (**6**)



(**1**) (**7**) (**8**)

The reaction of methyl cinnamate (**1**) with dichloromethane (**5**) (1:5 molar ratio) gave predominantly *trans*-methyl 2-phenylcyclopropanecarboxylate in high yield (87%). On the other hand, the electrochemical reduction of methyl cinnamate (**1**) with 1,4-dibromobutane (**7**) (1:3 molar ratio) produced *trans*-methyl 2-phenylcyclohexanecarboxylate as the main product (63%). The structure and the stereochemistry of the isolated cyclic products have been determined with satisfactory spectral and physical data.[9]

In conclusion, the presence of an aluminum acetate or an aluminum benzoate salt, produced in the system electrochemically, has increased the cyclic product yields in the electrochemical reduction of methyl cinnamate with dielectrophiles. Detailed work is being carried out in order to understand the mechanism of the cyclisation, whether a radical anion or dianion is involved in the cyclisation process, and the interaction of aluminum salts with these intermediates.

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7. Both cyclic products gave satisfactory spectroscopic and analytical results. **Product 3:** δ_H (400MHz; $CDCl_3$, TMS) 1.7-2.2 (6H, m, $3CH_2$), 2.82 (1H, q, J=9Hz), 3.34 (1H, q, J=9Hz), 3.6 (3H, s, $COO\underline{CH_3}$), 7.1-7.3 (5H, m, Ph): ν_{max} (KBr)/cm^{-1} 3060, 3029, 2952, 2873, 1732 (C=O ester), 1637, 1495, 1452, 1435, 1267, 1196, 1171, 739, 701; *m/z* 204, (M^+, %20, $C_{13}H_{16}O_2$, requires 204), 144 (100), 129 (18), 115 (30), 91 (40), 87 (54). **Product 4:** m.p. : 126-27°C, (Lit., m.p.: 126-27°C, Nishiguchi, I.; Hirashima, T.; *Angew. Chem., Int. Ed. Engl.*, **1983**, 22, 52.).
8. Stereochemistry of methyl 2-phenylcyclopentanecarboxylate was confirmed by hydrolysis of a small sample and the melting point of corresponding acid was of *trans*-isomer, m.p: 81-83°C (Lit.,m.p.: 82-84°C, Bordwell, F.G. and Almy, J., *J. Org. Chem.*,**1973**, 38, 574.
9. Satisfactory spectroscopic and analytical data were observed for both cyclic compounds (**6, 8**).
   Product 6: ν_{max} (KBr)/cm^{-1} 3029, 2952, 2878, 1730 (C=O ester) 1497, 1454, 1437, 1339, 1308, 1078. δ_H (400MHz; $CDCl_3$, TMS) 1.34 (1H, m), 1.64 (1H, m), 1.94 (1H, m), 2.57 (1H, m), 3.75 (3H, s, $COO\underline{CH_3}$) 7.1-7.3 (5H, m, Ph). *m/z* 176, (M^+, %30, $C_{11}H_{12}O_2$, requires 176), 162 (6) 144 (25), 115 (100), 91 (40). Corresponding carboxylic acid, prepared by basic hydrolysis was found to be the *trans* isomer of 2-phenylcyclopropancarboxylic acid, m.p: 85-86°C, (Lit.m.p.: 86-88°C, Aldrich Catalogue Handbook of Fine Chemicals, **1996-1997**, 1192). **Product 8:** ν_{max} (KBr)/cm^{-1} 3027, 2948, 2934, 1736 (C=O ester) 1495, 1454, 1437, 1258, 1165, 703. δ_H (400MHz; $CDCl_3$, TMS) 1.4-2.1 (8H, m, $4CH_2$), 2.6 (1H, m), 2.8 (1H, m), 3.4 (3H, s, $COO\underline{CH_3}$), 7.1-7.2 (5H, m, Ph). *m/z* 218, (M^+, %20, $C_{14}H_{18}O_2$, requires 218), 186 (15), 158 (100), 143 (10), 130 (30), 117 (35), 104 (25), 91 (85).