Turk J Chem
23 (1999) , 361 – 367.

Electrochemical Reduction of Methyl Cinnamate in the Presence of 1,3-Bis(4-methyl phenylsulphonyloxy)propane

Mustafa GÜLLÜ
Chemistry Department, Faculty of Sciences,
Ankara University, 06100, Tandoğan, Ankara-TURKEY

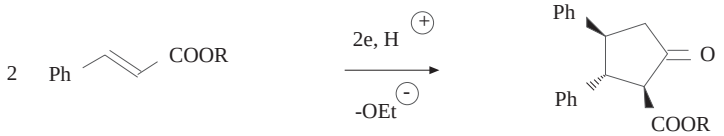
Received 07.04.1999

Electrochemical reduction of methyl cinnamate in the presence of a dielectrophile, such as 1,3-bis(4-methyl phenylsulphonyloxy)propane gives two major products: *trans*- (±) methyl 2-phenylcyclopentanecarboxylate and *trans*- (±) methyl 2,3-diphenyl-5-oxo-cyclopentanecarboxylate. The ratio of products basically depends on the electrolysis conditions.

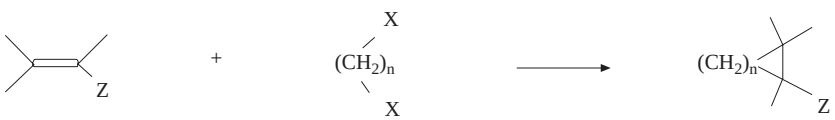
Key words: Methyl cinnamate, electrochemical reduction, cyclisation.

Introduction

Synthetically important three, five, and six membered cyclic compounds can be made by electrochemical reduction of activated alkenes. Cinnamate esters are known to form 2,3-diphenyl-5-oxo-cyclopentanecarboxylates exclusively by electrochemical reductive hydrodimerisation[1−2].



Cyclisation can also be established by the cross-coupling of electrochemically generated reactive intermediates of activated alkenes with different dielectrophiles[3−4]. Ring formation by this method has not been very succesful in a divided cell on a mercury cathode[3], but improved yields of cyclopropane and cyclopentane derivatives were observed in the presence of electrochemically formed metal ions with a sacrificial anode in an undivided cell[4].



Z: Electron Withdrawing Group

X=Cl,Br
n=1-4

Although a wide selection of alkenes and dihalides produced corresponding cyclic derivatives, because of the low product yield the method is still far from synthetic utilisation. Therefore, the coupling reaction of activated alkenes has been studied to improve the product selectivity and product yields. In this study, electrochemical reduction of methyl cinnamate **(1)** in the presence of a more reactive dielectrophile, 1,3-bis(4-methyl phenylsulphonyloxy)propane **(2)** was examined as a probe reaction in order to determine the selectivity in the coupling reactions of activated alkenes.

Experimental

^{1}H nmr spectra were recorded with a Bruker G-MbH-DpX Model (400MHz) sepctrometer. Infrared spectra were recorded on a Mattson 100 FTIR spectrometer. GC-MS analyses were performed with a Hewlett Packard HP6890 GC/HP6890 Mass Selective Detector/HP5972 MSD system on a HP-5MS (cross linked 5%PH ME Siloxane) type capillary column. Cyclic voltammetry and constant potential electrolyses were performed with an ENTEK PGS2000 Model Potentioscan instrument.

Solvents [acetonitrile (MeCN), N,N-dimethyl formamide (DMF) and 1-methyl-2-pyrrolidione (NMP)] and supporting electrolytes [tetraethylammonium bromide (TEABr), tetrabutylammonium tetrafluoroborate (TBAF), tetrabutylammonium bromide (TBABr), and lithium perchlorate ($LiClO_4$)] were used after purification according to the usual procedures. All other reagents were purified in an appropriate method (distillation or re-crystallisation). The sacrificial anode was of 99.99% purity and was used without any cleaning of the oxide film on the metal surface.

Synthesis of 1,3-bis(4-methyl phenylsulphonyloxy)propane (2);

Propane-1,3-diol (0.04mol, 3ml) was dissolved in triethylamine (0.1mol, 14ml) and added dropwise to the solution of 4-methyl phenylsulphonyl chloride (0.09mol, 17.5g) in dichloromethane (40 ml), while cooling the solution with an ice bath. This mixture was stirred over 3h and separated from $Et_3NH^+Cl^-$ salt by filtering and washing with dichloromethane (20ml). The final solution was washed with 1N HCl, saturated Na_2CO_3 solution and water and dried on Na_2SO_4. The crude residue recovered after evaporation of dichloremethane was re-crystallised from ethanol. Yield : 15.0g (98%), m.p : 90-92°C(Lit[5]. m.p. : 90-92°C).

Electrolyses

Three different methods were used for the electrolysis of methyl cinnamate (1) in the presence of 1,3-bis(4-methyl phenylsulphonyloxy) propane (2). The general conditions applied in these three methods are described below.

Method A - Electroreduction of methyl cinnamate(1) in the presence of 1,3-bis(4-methyl phenylsulphonyloxy) propane (2) in a divided cell :

A solution (45ml) of supporting electrolyte (0.1M) in an appropriate solvent was prepared and put into the cathode and the anode compartments of a divided electrolysis cell. This solution was pre-electrolysed at -2,0V (vs.Ag/Ag^+) until the cell current dropped to a value lower than 2-3mA, under a slow stream of nitrogen using mercury as the cathode (surface area 12cm^2), graphite as the anode and Ag/Ag^+ as the reference electrode. Methyl cinnamate **(1)** (0.004mol, 0.65g) and 1,3-bis(4-methyl phenylsulphonyloxy)propane **(2)** were introduced into the catholyte compartment of the electrolysis cell and electrolysed at -1.7V to -1.9V until 2.7-3F/mol charge consumption. The resulting catholyte solution was poured into a cold 1N

HCl (200ml) solution. Organic materials were extracted with diethyl ether (2×50ml), which was washed with saturated Na_2CO_3 solution and water, then dried on Na_2SO_4. After evaporation of the solvent, the crude product was purified by column chromatogray using silica gel (230 mesh) and hexane/diethyl ether (4:1). Two major compounds were isolated and identified. Their yields were found to be affected by the experimental conditions and the results are given in table 2.

trans (±) **methyl 2-phenylcyclopentane carboxylate (3):**

ν**max (KBr)/cm**$^{-1}$ 3060, 3029, 2952, 2873, 1732 (C=O ester), 1637, 1495, 1452, 1435, 1267, 1196, 1171, 701. $\delta_{\mathbf{H}}$ **(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, COCO$\underline{CH_3}$), 7.1-7.3 (5H, m, Ph). **m/z** 204, (M^+, 20%, $C_{13}H_{16}O_2$, calculated m.:204), 144 (100), 129 (18), 115 (30), 91 (40). The *trans* stereochemistry of this compound was established by alkaline hydrolysis of an authentic sample and structural identification of the free carboxylic acid **(4)**.

M.p. : 80-83°C (Lit[6]. m.p.: 82-84°C, *trans* -isomer). ν**max (KBr)/cm**$^{-1}$ 3250-2539 (broad, COOH), 3025, 2948, 1699 (C=O acid), 1630, 1493, 1450, 1421, 1287, 1227, 936, 703. $\delta_{\mathbf{H}}$ **(400MHz; CDCl$_3$, TMS)** 1.7-2.2 (6H, m, $3CH_2$), 2.82 (1H, q, J=9Hz), 3.4 (1H, q, J=9Hz), 7.1-7.3 (5H, m, Ph).

trans(±) **methyl 2,3-diphenyl-5-oxo-cyclopentanecarboxylate (5):**

M.p. : 126-9°C (Lit[1]. m.p.: 127-9°C). ν**max (KBr)/cm**$^{-1}$ 3012, 2954, 2865, 1750 (C=O ester), 1710 (C=O ketone), 1450, 1272, 1250, 1120. $\delta_{\mathbf{H}}$ **(400MHz; CDCl$_3$, TMS)** 2.75 (1H, dd), 2.99 (1H, dd), 3.52 (1H, m), 3.63 (1H, d), 3.75 (3H, s), 3.95 (1H, t), 7.1-7.35 (10H, Ph). **m/z 236 [M^+- 58 ($COOCH_3$), 35%, $C_{19}H_{18}O_3$, calculated m.:294],** 208 (3), 178 (6), 115 (8), 104 (100), 91 (4), 78 (20), 51 (10).

Two more compounds were identified by GC-MS analysis as methyl hydrocinnamate **(6)**, and methyl 3-phenyl 5-hexenoate, but they could not be isolated in a purer state due to their low yields.

Method B - Electroreduction of methyl cinnamate (1) and 1,3-bis(4-methyl phenylsulphonyloxy)propane (2) in an undivided cell with a sacrificial anode :

A solution (10ml) of supporting electrolyte (0.1M) in an appropriate solvent was prepared and put into an undivided electrolysis cell. This solution was pre-electrolysed at -2.0V (vs.Ag/Ag^+) until the cell current dropped to a value lower than 2-3mA, under a slow stream of nitrogen using stainless steel as the cathode (surface area 10cm^2), aluminium as the sacrificial anode and Ag/Ag^+ as the reference electrode. Methyl cinnamate **(1)** (0.002mol, 0.324g) and 1,3-bis(4-methyl phenylsulphonyloxy)propane **(2)** were introduced into the catholyte compartment of the electrolysis cell and electrolysed at -1.7V to -1.9V until 3-3.5F/mol charge consumption. Following the electrolysis, isolation of the crude product was carried out as described above. Two major compounds, *trans*-(±) methyl 2-phenylcyclopentanecarboxylate **(3)** and *trans*-(±) methyl 2,3-diphenyl-5-oxo-cyclopentanecarboxylate **(5)** were isolated and identified by spectral means and found to be consistent. Isolated product yields are given in table 2.

Method C - Electroreduction of methyl cinnamate (1) and 1,3-bis(4-methyl phenylsulphonyloxy)propane (2) in an divided cell in the presence of electrochemically formed aluminium carboxylates :

A solution (10ml) of supporting electrolyte (0.1M) in an appropriate solvent was prepared and put into an undivided electrolysis cell. This solution was added an appropriate amount of a carboxylic acid (acetic or benzoic acid) and electrolysed at -1,6V (vs.Ag/Ag^+) until the cell current dropped to a value lower than 15 mA, under a stream of nitrogen using stainless steel as the cathode (surface area 10cm^2), aluminium as the sacrificial anode and Ag/Ag^+ as the reference electrode. After formation of an aluminium carboxylate salt, the Al anode was replaced with a graphite anode. Then methyl cinnamate **(1)** (0.002mol, 0.324g) and 1,3-bis(4-methyl phenylsulphonyloxy)propane **(2)** were introduced into the electrolysis cell and

electrolysed at -1.7V to -1.9V until 3-3.5F/mol charge consumption.

Following the electrolysis, the same work-up was applied as described above. Two major compounds; *trans*-(±) methyl 2-phenyl cyclopentanecarboxylate **(3)** and *trans*-(±) methyl 2,3-diphenyl-5-oxo-cyclopentanecarboxylate **(5)** were isolated and identified by spectral means and found to be consistent. Isolated product yields are given in table 2.

Results and Discussion

Electrochemical reduction of methyl cinnamate **(1)** in the presence of 1,3-bis(4-methyl phenylsulphonyloxy)propane (BTP) **(2)** was studied in different experimental conditions in order to improve the cross-coupling product yield. Preliminarily, cyclic voltammetry experiments were carried out with cinnamates and 1,3-bis(4-methyl phenylsulphonyloxy)propane **(2)** and the results are given in table 1.

Table 1. Cyclic voltammetry results $^{(\star)}$

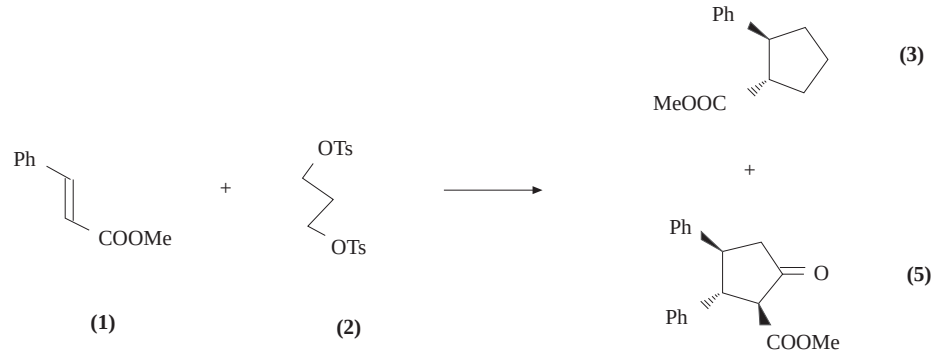
Substrate	**Ep,c**^{1}	**Ep,c**^{2}
Methyl cinnamate **(1)**	-1.30V(qr)$^{(\star\star)}$	-1.85V(irr)
Ethyl cinnamate **(7)**	-1.35V(qr)$^{(\star\star)}$	-1.95V(irr)
BTP **(2)**	-2.20V(irr)	–
Methyl cinnamate + BTP **(1/1)**	-1.70V(irr)	–

($\star$) Cyclic voltammetry experiments were carried out in the anhydrous DMF/TEABr solvent-electrolyte system using a Pt bead cathode, a Pt anode and a Ag/Ag^+ reference electrode. Sweep rate is 300mV/s, irr: irreversible.

($\star\star$) qr: Quasi reversible electron transfer, reversible at high sweep rates ($>$500mV/s) and irreversible at low sweep rates ($<$50mV/s).

The reduction of 1,3-bis(4-methyl phenysulphonyloxy)propane **(2)** takes place at more negative potentials, which indicates its stability towards an electrochemical reaction at the reduction potentials of cinnamate esters. It was expected that the first electron transfer would take place with the cinnamate ester, and the resulting reactive intermediates can undergo expected coupling reaction with 1,3-bis(4-methyl phenylsulphonyloxy)propane **(2)**.

Controlled potential electrolyses of methyl cinnamate **(1)** in the presence of 1,3-bis(4-methyl phenylsulphonyloxy)propane **(2)** were carried out in different experimental conditions. In all cases, the yields of two major compounds; *trans*-(±) methyl 2-phenyl cyclopentanecarboxylate **(3)** and *trans*-(±) methyl 2,3-diphenyl-5-oxo-cyclopentane carboxylate **(5)** were monitored. Because the electrode potential and current density slightly affect the product ratio, electrolyses were carried out at a controlled potential around -1.7V to -1.9V. The molar ratio of methyl cinnamate **(1)** and 1,3-bis(4-methyl phenylsulphonyloxy)propane **(2)** was kept at 1:3 in favour of cross-coupling reaction. The results of the electrolyses are briefly summarised in table 2.



(1) **(2)** **(3)** **(5)**

The cross-coupling product of methyl cinnamate **(1)** with 1,3-bis(4-methylphenyl sulphonyloxy)propane **(2)**, *trans*-(±) methyl 2-phenylcyclopentanecarboxylate **(3)** was the less favoured product in a divided cell at a mercury cathode, where *trans*-(±) methyl 2,3-diphenyl-5-oxo-cyclopentane carboxylate **(5)** was the dominant one. The better solvent-supporting electrolyte system was observed to be DMF/TEABr as shown in table 2. The presence of a small cation like Li^+ ($LiClO_4$) increased the formation of cyclic hydrodimer, *trans*-(±) methyl 2,3-diphenyl-5-oxo-cyclopentane carboxylate **(5)**. On the other hand, the presence of a metal cation like Al^{+3}, Zn^{+2}, Fe^{+3} resulted in polymer formation and caused electrode passivation. 1,3-Bis(4-methyl phenylsulphonyloxy)propane **(2)** was undesirably decomposed under the sacrificial aluminium anode conditions in an undivided cell, but some cyclic hydrodimer formation was also observed.

Table 2. The Effect of Electrolyses Conditions on the Product Selectivity

No	**Solvent**	**Electrolyte**	**Method-Acid (M)**	**Product 3** (%)	**Product 5** (%)
1	DMF	TEABr	A	20	50
2	DMF	$LiClO_4$	A	-	72
3	MeCN	TBABF	A	-	45
4	NMP	TBABF	A	-	-
5	DMF	TEABr	B	-	25
6	DMF	TEABr	A[1)]	-[2)]	-[2)]
7	DMF	TEABr	A[3)]	-[2)]	-[2)]
8	DMF	TEABr	C-Acetic (2)	-[2)]	-[2)]
9	DMF	TEABr	C-Acetic (0.2)	14	34
10	DMF	TEABr	C-Acetic (0.02)	44	12
11	DMF	TEABr	C-Acetic (0,01)	40	15
12	DMF	TEABr	C-Benzoic (0.02)	46	25
13	DMF	TEABr	C-Benzoic (0.01)	37	20

1) In the presence of 0.2M $AlBr_3$.

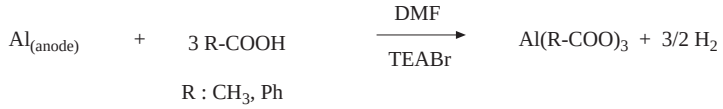
2) Electrode passivation due to polymer formation.

3) In the presence of 0.1 M $ZnCl_2$.

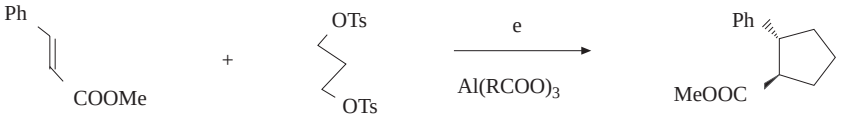
The highest yield of cross-coupling product was achieved in the presence of a catalytic amount of electrochemically-formed aluminium carboxylate salt. A carboxylic acid, acetic acid or benzoic acid was pre-electrolysed under sacrificial anode conditions, then substrate and reagent were electrolysed in this solution. The amount of the salt dramatically changed the product distribution; in high salt concentrations (2M) the reaction occurred as if sacrificial anode conditions had been applied, whereas in lower concentrations of the salt

(0.01-0.02M) the formation of cross-coupling product, *trans*-(±) methyl 2-phenylcyclopentanecarboxylate **(3)** was favoured.

Pre-electrolysis:

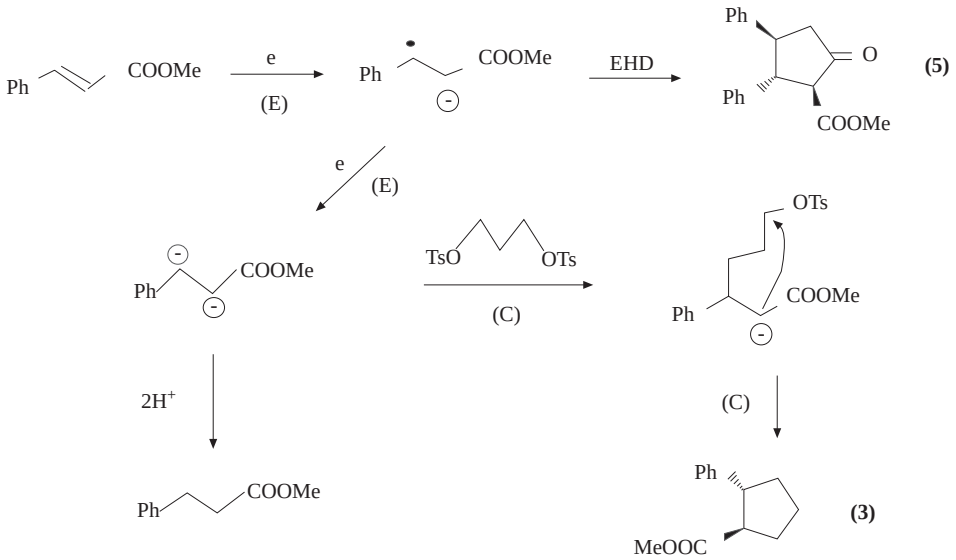


Electrolysis:



(1) **(2)** **(3)**

The results obtained in both divided and undivided electrolyses conditions indicate that the cross-coupling reaction takes place via a dianion intermediate. Since the cyclic hydrodimer formation occurs by the coupling of radical-anions formed with one electron transfer, conditions leading to a dianion intermediate favours the cross-coupling reaction between the dianion of activated alkene and dielectrophile, as observed from these experimental results. An EECC mechanism for the cross-coupling can be suggested in light of these results.



Conclusion

Electrochemical cyclisation of methyl cinnamate **(1)** with 1,3-bis(4-methylphenyl sulphonyloxy)propane **(2)** was investigated. Although expected high yields of *trans*-(±) methyl 2-phenylcyclopentanecarboxylate **(3)** could not be achieved, a systematic study of the reaction was realised. These results clearly indicate the necessity of a two-electron transfer process for the formation of a dianion, which is the key intermediate in the cross-coupling reaction. Nevertheless, conditions required for the dianion formation were observed

to be harmful for the dielectrophile used. 1,3-Bis(4-methylphenyl sulphonyloxy)propane **(2)** can easily be deactivated by decomposition in the presence of equimolar amounts of a metal cation like Al^{+3}. On the other hand, if the metal cation is used strictly in catalytic amounts, it is possible to increase the yield of cross-coupling product, *trans*-(±) methyl 2-phenylcyclopentanecarboxylate **(3)**.

Acknowledgment

I wish to thank The Scientific and Technical Research Council of Turkey (TÜBİTAK) for financially supporting this project (TBAG-1344).

References

1. M. Güllü, "Electrochemical Dimerisations of Pyrido[1,2-a]pyrimidines and of Cinnamates" Ph.D. Thesis, University of London, London, UK, 1993.
2. J. H. P. Utley, M. Güllü, M. Motevalli, *J. Chem. Soc. Perkin Trans. I.,* 1961-1970, (1995).
3. C. Degrand, P. L. Compagnon, G. Belot, D. Jacquin, *J. Org. Chem.,* **45**, 1189-1196, (1980).
4. Y. W. Lu, J. Y. Nedelec, J. C. Folest, J. Perichon, *J. Org. Chem.,* **55**, 2503-2507, (1990).
5. Aldrich Catalogue Handbook of Fine Chemicals, 1240 (1994-1995).
6. F. G. Bordwell, J. Almy, *J. Org. Chem.,* **38**, 0574-579, (1973).