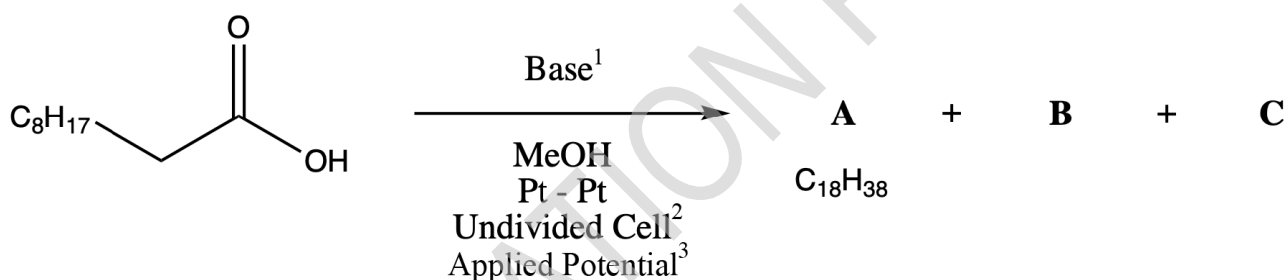


Electrolysis in Organic Synthesis

6% of total								
Question	9.1	9.2	9.3	9.4	9.5	9.6	9.7	Total
Points	3	3	2	5	5	2	9	29
Score								

The Kolbe electrolysis describes the decarboxylative dimerization of two carboxylic acids and only proceeds if the acid is deprotonated. The unbalanced equation is shown here.



Translations:

1:

2:

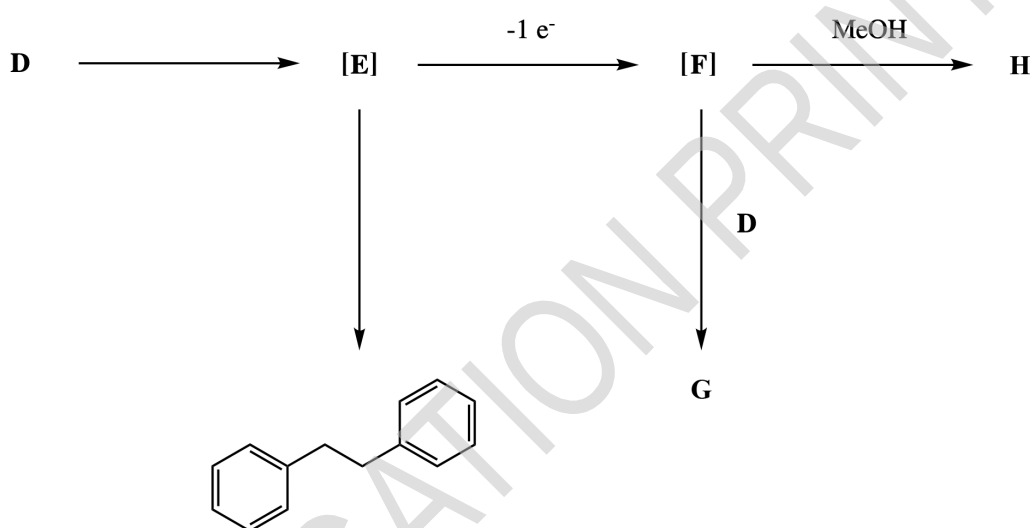
3:

Two gases (**B** and **C**) are produced during the reaction. **B** reacts with $\text{Ca}(\text{OH})_2$, while **C** is highly flammable.

9.1	Provide the structural formulae of A , B , and C .	3pt
9.2	The synthesis is formally a redox reaction, where the carboxylate is oxidized and the solvent is reduced. Formulate the oxidative and reductive half reactions and the full redox reaction.	3pt
9.3	Provide the intermediates in the mechanism for the oxidative decarboxylation and formation of the product.	2pt

The Kolbe electrolysis is usually only efficient for long-chained saturated carboxylic acids and not for certain carboxylic acids, such as **D**. Here, the overoxidation of the radical intermediate **E** to a positively charged species **F** is facilitated.

Intermediate **F** can react with nucleophiles to form different side products, for example it reacts with **D** to form an ester **G**, and with MeOH to form **H**.



9.4 Provide the structures of **D-H**.

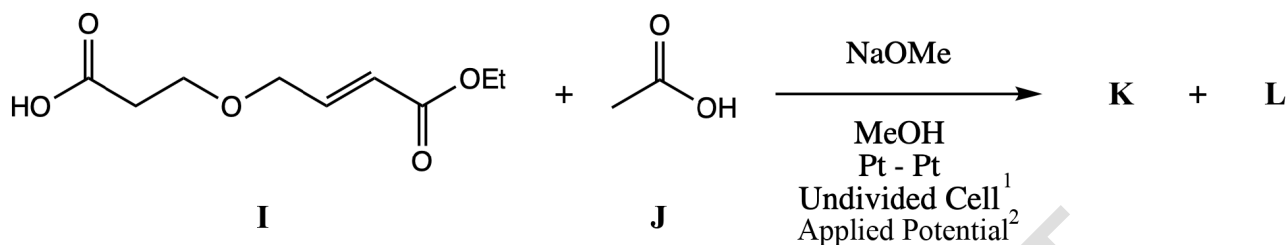
5pt

The electrolysis of carboxylic acid **I** in the presence of an excess of co-acid **J** yields two main products (by ¹H NMR analysis) that are inseparable by silica gel chromatography. Their spectroscopic data are almost identical. In the ¹H NMR spectrum, the two species are only distinguishable by two signals with small differences in chemical shifts. The spectrum looks as follows (1:1 mixture of products):

¹H NMR (**K** and **L**): 4.18 – 4.08 (m, 4 H), 3.95 – 3.60 (m, 6 H), 3.43 (dt, 2 H, $J = 7.8, 2.2$ Hz), 2.55 – 2.25 (m, 4 H), 2.20 – 1.95 (m, 2 H), 1.65 – 1.50 (m, 2 H).

Specific signals for **K**: 1.26 (t, 3 H, $J = 7.2$ Hz), 1.20 (d, 3 H, $J = 6.6$ Hz).

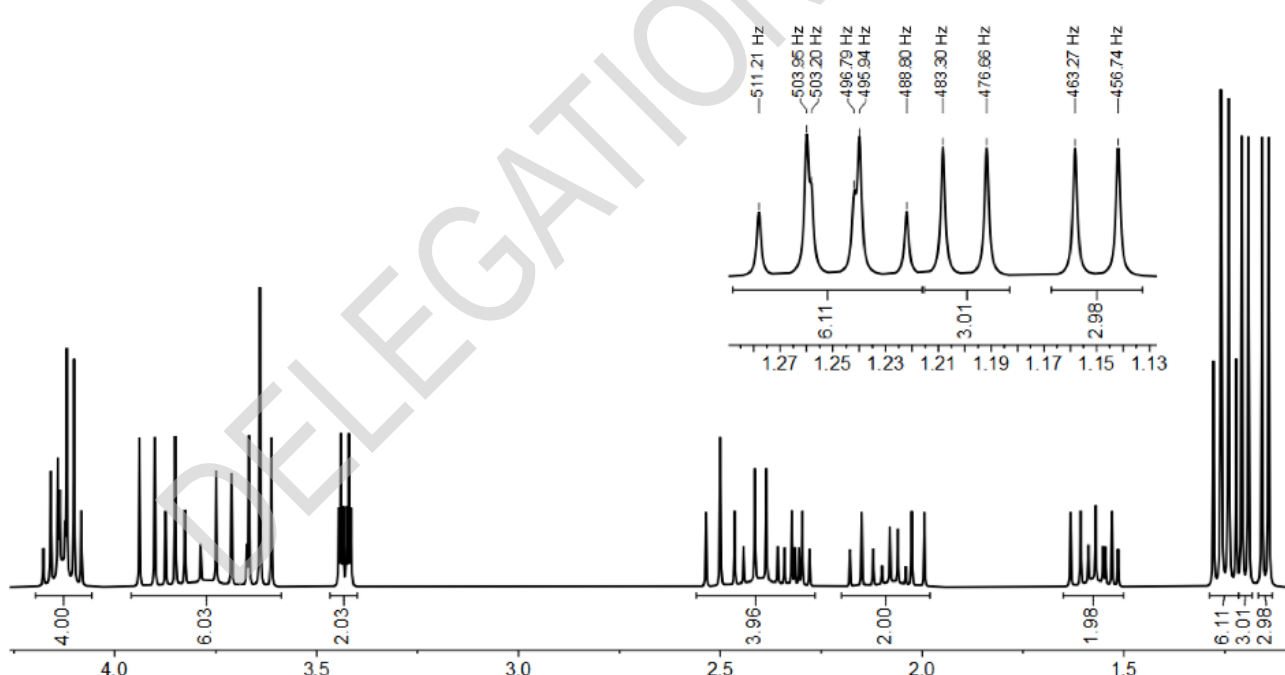
Specific signals for **L**: 1.24 (t, 3 H, $J = 7.2$ Hz), 1.15 (d, 3 H, $J = 6.6$ Hz).



Translation:

1:

2:



9.5 Provide the structures for both products **K** and **L**. Indicate how the two products are related. 5pt

The choice of the electrode material can influence the selectivity of an organic electrochemical reaction. The reductive electrolysis of benzaldehyde (**M**) (16 mM in 1 M aqueous KOH, Pt anode, -1.3 V vs. Ag/AgCl) yields different products depending on the cathode material used. Strong binding to the surface favours intermolecular reactions. The figure below shows the product distribution for different cathode materials and the mass spectra of the products.

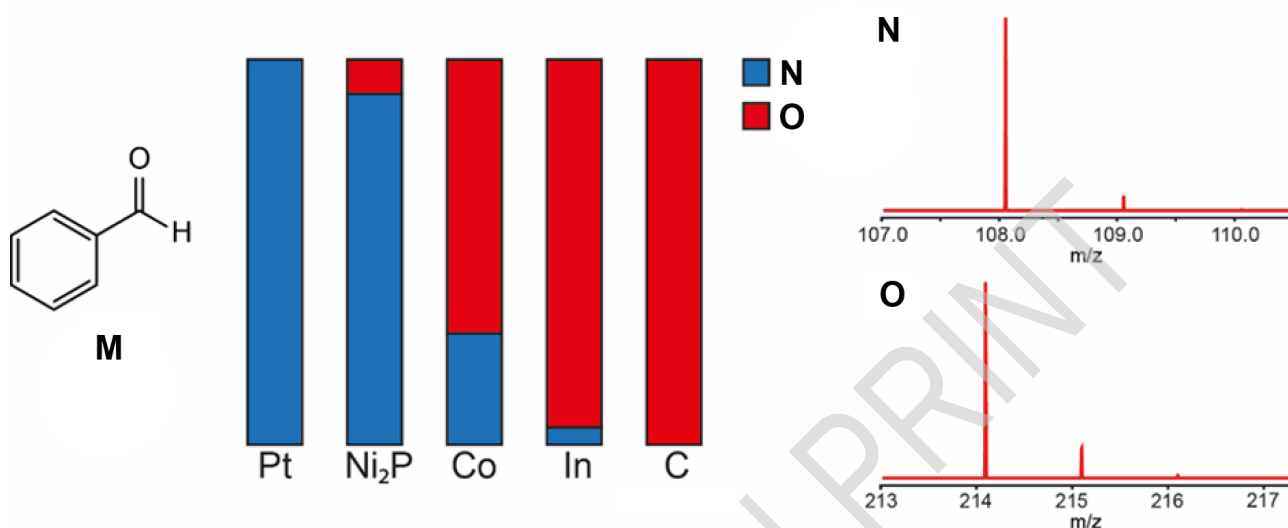
Theory



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Q9-4

English (Official)



9.6 Provide the structure of **N** and **O**.

2pt

Alkenes, such as enol ethers, can be oxidatively coupled. This typically involves the anodic oxidation of the alkene fragment to yield a radical cation which can be intercepted by a nucleophile.

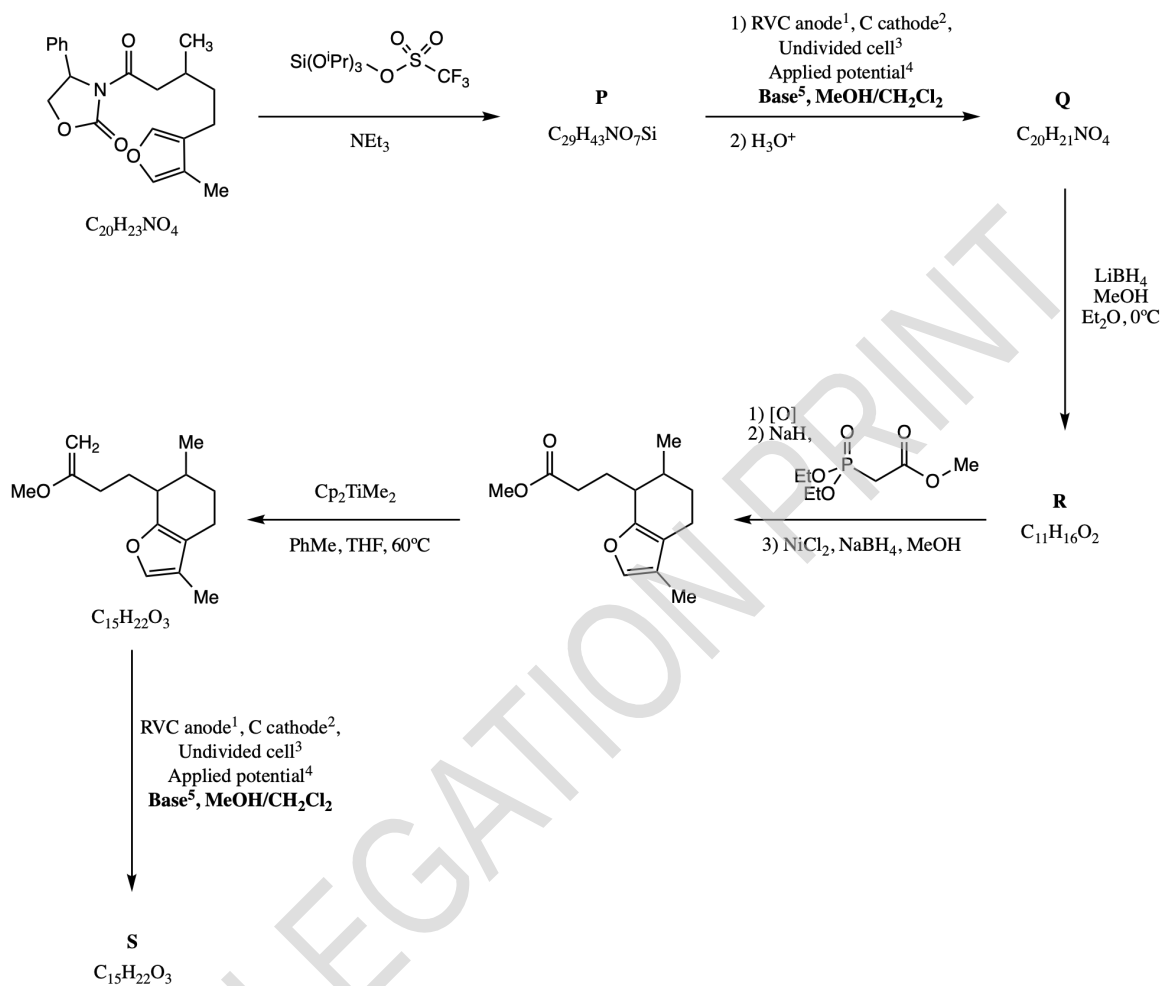
Theory



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English (Official)



Translation:

1: RVC = glassy carbon

2:

3:

4:

5:

Cp = cyclopentadienyl

Theory



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Q9-6

English (Official)

- 9.7 **Provide** the structural formulae of compounds **P**, **Q**, **R**, and **S**. Indicating stereochemistry is not required. *Hint: S* is a tricyclic product. 9pt

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