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OCA PAD INITIATION - PROJECT HEADER INFORMATION

04/24/95

Active

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Center # : 10/24-6-R8479-0A0 Center shr #: OCA file #:
Contract#: AGR DTD 950331 Mod #: Work type : RES
Prime # : Document : AGR
Contract entity: GTRC

Subprojects ? : N CFDA:
Main project #: PE #:

Project unit: CHEMISTRY Unit code: 02.010.136
Project director(s):
 BOTTOMLEY L A CHEMISTRY (404)894-4014

Sponsor/division names: HOECHST CELANESE CORP / CHARLOTTE, NC
Sponsor/division codes: 207 / 013

Award period: 950401 to 950930 (performance) 950930 (reports)

Sponsor amount	New this change	Total to date
Contract value	41,377.00	41,377.00
Funded	41,377.00	41,377.00
Cost sharing amount		0.00

Does subcontracting plan apply ? : N

Title: INDIRECT ELECTROSYNTHESIS OF ALPHA-KETO ACETALS

PROJECT ADMINISTRATION DATA

OCA contact: E. Faith Gleason 894-4820

Sponsor technical contact Sponsor issuing office

RICARDO E. BORJAS
(512)242-4000

KENNETH G. DAVENPORT
(512)242-4000

HOECHST CELANESE CORPORATION
P.O. BOX 9077
CORPUS CHRISTI, TX 78469-9077

HOECHST CELANESE CORPORATION
P.O. BOX 9077
CORPUS CHRISTI, TX 78469-9077

Security class (U,C,S,TS) : U
Defense priority rating :
Equipment title vests with: Sponsor

ONR resident rep. is ACO (Y/N): N
supplemental sheet
GIT

Administrative comments -

* INITIATION.

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Georgia Institute of Technology
Office of Contract Administration
PROJECT CLOSEOUT - NOTICE

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Closeout Notice Date 07-OCT-1997

Project Number G-33-E90

Doch Id 36767

Center Number 10/24-6-R8479-0A0

Project Director BOTTOMLEY, LAWRENCE

Project Unit CHEMISTRY

Sponsor HOECHST CELANESE CORP/CHARLOTTE, NC

Division Id 4107

Contract Number AGR DTD 950331

Contract Entity GTRC

Prime Contract Number

Title INDIRECT ELECTROSYNTHESIS OF ALPHA-KETO ACETALS

Effective Completion Date 30-SEP-1995 (Performance) 30-SEP-1995 (Reports)

Closeout Action:	Y/N	Date Submitted
Final Invoice or Copy of Final Invoice	N	
Final Report of Inventions and/or Subcontracts	Y	
Government Property Inventory and Related Certificate	N	
Classified Material Certificate	N	
Release and Assignment	N	
Other	N	

Comments

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Distribution Required:

Project Director/Principal Investigator	Y
Research Administrative Network	Y
Accounting	Y
Research Security Department	N
Reports Coordinator	Y
Research Property Team	Y
Supply Services Department	Y
Georgia Tech Research Corporation	Y
Project File	Y

NOTE: Final Patent Questionnaire sent to PDPI

Indirect Electrosynthesis of alpha-Keto Acetals

A progress report

Prepared by:

**Lawrence A. Bottomley
Professor of Chemistry
Georgia Institute of Technology
Atlanta, GA 30332-0400**

and

**Jack Winnick
Professor of Chemical Engineering
Georgia Institute of Technology
Atlanta, GA 30332-0100**

and submitted to:

**Ricardo E. Borjas
Analytical Group
Hoechst Celanese Corporation
Corpus Christi Technical Center
Corpus Christi, TX 78469**

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Research Plan

Phase I. The characterization of the electrochemical behavior of all components (in both Karcher's and Chandalia's method) for converting arylmethyl ketones to α -keto acetals using cyclic and rotating-ring-disk voltammetry was the primary aim of this initial phase. Special emphasis was to be placed on identifying appropriate electrode materials, solvents and potential windows where the arylmethyl ketone reactant and the phenylgloxal and α -keto acetal products were electroinactive and where the selenium-based reactants were electroactive.

Phase II. We proposed the construction of a laboratory-scale electrochemical reactor for the electrosynthesis of α -keto acetals in both the controlled potential and current modes. We proposed to determine product distributions using gas chromatography/mass selective detection.

Phase III. The fabrication of a bench-scale reactor with high surface area electrodes was proposed. From the results of initial batch runs with this cell, a cost model will be developed for the electrocatalytic conversion of arylmethyl ketones to α -keto acetals.

Work Accomplished

Phase I. We evaluated the electrooxidative behavior of each of the following compounds in methanol solution at both a Pt and graphite anode: acetophenone (AP), 4-hydroxyacetophenone (4-HAP), 1-acetonaphthone (1-AN), 2-acetonaphthone (2-AN), 4-methoxyacetophenone (4-MAP), sodium bromide, p-toluenesulfonic acid, lithium perchlorate, and diphenyldiselenide. We have synthesized the α -keto acetals of AP, 2-AN, 1-AN, 4-HAP and 4-MAP chemically according to Tiecco's method and verified purity by ^1H nmr spectroscopy and mass spectrometry. The spectral results are summarized in Table 1. These materials were used as thin layer chromatographic standards.

Phase II. We have carried out electrooxidations of 2-AN using a two electrode cell and systematically determined the importance of the following factors on product and byproduct yields:

- electrolysis time (under controlled current)
- controlled current vs. controlled potential
- concentration of p-toluenesulfonic acid (0 to 0.5 M)
- concentration of diphenyldiselenide (0 to 0.075 M)
- effect of undivided versus divided cell (porous frit, Nafion 117 membrane, Nafion 450 membrane)
- concentration and identity of supporting electrolyte (NaBr, KSCN, NaClO_4 , LiClO_4 , KBF_4 , TEABF_4 , NaOAc , HOAc/NaOAc).

We have monitored the course of these reactions with thin layer chromatography and characterized the reaction products with ^1H nmr and gas chromatography with mass selective detection both before and after product separation on a preparative scale silica gel column.

The results of this phase of the investigation are summarized as follows:

- Under controlled current, the desired α -keto acetal product first increases and then decreases with time. The decrease is associated with oxidation of the α -keto acetal product to the acid.
- The fewest number of components are found in the product mixture when the electrolysis is carried out under controlled potential. This electrolysis method necessitated a longer electrolysis time. The rate of electrolysis may be increased through the use of high-surface area anodes to be explored in phase III of this investigation.
- When diphenyldiselenide is in the reactant mixture, the α -keto acetal product is obtained. The only exception is when sodium acetate is used as the supporting electrolyte.
- The product yield, number of intermediates and number of byproducts is strongly dependent upon the concentration of diphenyldiselenide, the electrolyte used, the electrolysis time and whether a divided cell is used. The intrinsic resistance of the divider necessitated higher applied potentials.
- Except in the case of 4-HAP, the formation of product appears independent of the amount of p-toluenesulfonic acid present in the reactant mixture.
- The amount of α -keto acetal is markedly dependent upon the identity of the supporting electrolyte. The results obtained for this particular study are summarized in Table 2.
- In some instances, the process appears to be electrocatalytic, but we have not yet determined turnover numbers.
- The α -keto acetal product is formed at either a Pt or graphite anode. Since there is a significant difference in cost between the two anode materials, a porous graphite electrode would appear to be preferable.

We have electrooxidized AP, 1-AN, 4-HAP and 4-MAP using the best conditions found for the production of 2-AN-ka. The conditions and product compositions are summarized in Table 3. Selected gas chromatograms and mass spectral analyses are included as an appendix to this report. Additional spectra and chromatograms are available upon request. The results of this phase of the investigation are:

- The desired α -keto acetal products are prepared in ~ 75% yield with the electrooxidative method used. No attempt has been made to optimize the yield; the values reported are likely to be conservative estimates of the yield obtainable from this method.
- The production of the α -keto acetal of 4-HAP requires an acidic environment to keep the phenolic group protonated.
- It was anticipated that the use of a bromide containing supporting electrolyte would facilitate the electrocatalytic formation of the α -keto acetal via electrooxidation of bromide at the electrode followed by homogeneous reduction with diphenyldiselenide. However, this was not observed. Instead, α -brominated methyl ketones were found in the product mixtures.

Phase III. Preliminary cost models have been formulated based on the yield estimates. These suggest that the desired α -keto acetal products can be produced electrochemically at a significant profit. We are currently attempting to increase yields and reduce cell voltages by minimizing the resistance of both the solution and the divider, increasing and regulating the rate of mass transfer and increasing the surface area of both the anode and cathode. We are also designing a bench-scale reactor with high surface area electrodes for use in phase III experiments. We are exploring ways to immobilize the Se-based oxidant/catalyst (e.g. diphenyldiselenide or SeO_2) to eliminate the need for removal of the selenium-byproducts from the product stream.

TABLE 1. CHARACTERIZATION OF REAGENTS AND PRODUCTS

Compound (abbreviation)	Formula (vendor)	Description	¹ H NMR spectrum	Mass spectrum
acetophenone (AP)	C ₆ H ₅ COCH ₃ (Aldrich)	colorless liquid	2.61 (s, 3H) 7.4-7.5 (m, 2H) 7.5-7.6 (m, 1H) 7.9-8.0 (m, 2H)	120 (M+), 105 (base), 91, 77, 63, 51, 43
acetophenone α- keto acetal (AP-ka)	C ₆ H ₅ COCH(OCH ₃) ₂ (synthesized using Tiecco's method and GaTech's electrochemical method)	light orange oil	3.48 (s, 6h) 5.24 (s, 1H) 7.4-7.55 (m, 2H) 7.55-7.7 (m, 1H) 8.1-8.2 (m, 2H)	149 (M+), 121, 105, 91, 75, (base), 51, 47
1-aceto-naphtho- phenone (1-AN)	C ₁₀ H ₇ COCH ₃ (Aldrich)	colorless liquid	2.76 (s, 3H) 7.4-7.7 (m, 2H) 7.8-8.1 (m, 4H) 8.7-8.8 (m, 1H)	170 (M+), 155 (base), 127, 77, 63, 43
1-acetonaph- thophenone α- keto acetal (1-AN-ka)	C ₁₀ H ₇ COCH(OCH ₃) ₂ (synthesized using Tiecco's method and GaTech's electrochemical method)	light yellow oil	3.52 (s, 6H) 5.31 (s, 1H) 7.5-7.7 (m, 3H) 7.85-7.95, (m, 1H) 8.0-8.1 (m, 1H) 8.2-8.3 (m, 1H) 8.65-8.75 (m, 1H)	230 (M+), 199, 167, 155, 139, 137, 75 (base), 47
2-aceto-naphtho- phenone (2-AN)	C ₁₀ H ₇ COCH ₃ (Aldrich)	white solid	2.74 (s, 3H) 7.5-7.7 (m, 2H) 7.8-8.15 (m, 4H) 8.48 (s, 1H)	170 (M+), 155 (base), 127, 101, 77, 63, 43
2-acetonaph- thophenone α- keto acetal (2-AN-ka)	C ₁₀ H ₇ COCH(OCH ₃) ₂ (synthesized using Tiecco's method and GaTech's electrochemical method)	light yellow oil	3.52 (s, 6H) 5.37 (s, 1H) 7.5-7.7 (m, 2H) 7.8-8.2 (m, 4H) 8.74 (s, 1H)	230 (M+), 201, 171, 155, 127, 75 (base), 47
4-hydroxyace- tophenone (4-HAP)	HOC ₆ H ₄ COCH ₃ (Aldrich)	white solid	2.58 (s, 3H) 6.9-7.0 (m, 2H) 7.9-8.0 (m, 2H) >10.0 (s, 1H)	136 (M+), 121 (base), 93, 65, 43, 39

4-hydroxyacetophenone α -keto acetal (4-HAP-ka)	$\text{HOC}_6\text{H}_4\text{COCH}(\text{OCH}_3)_2$ (synthesized using Tiecco's method and GaTech's electrochemical method)	light violet oil	3.46 (s, 6H) 5.31 (s, 1H) 6.9-7.0 (m, 2H) 8.05-8.15 (m, 2H) >10.0 (s, 1H)	196 (M+), 137, 121, 93, 75 (base), 65, 47
4-methoxyacetophenone (4-MAP)	$\text{CH}_3\text{OC}_6\text{H}_4\text{COCH}_3$ (Aldrich)	white crystal	2.57 (s, 3H) 3.88 (s, 3H) 6.9-7.0 (m, 2H) 7.9-8.0 (m, 2H)	150 (M+), 135 (base), 107, 92, 77, 64, 43
4-methoxyacetophenone α -keto acetal (4-MAP-ka)	$\text{CH}_3\text{OC}_6\text{H}_4\text{COCH}(\text{OCH}_3)_2$ (synthesized using Tiecco's method and GaTech's electrochemical method)	white crystals	3.47 (s, 6H) 3.88 (s, 3H) 5.19 (s, 1H) 6.9-7.0 (m, 2H) 8.1-8.2 (m, 2H)	210 (M+), 179, 151, 135, 92, 75 (base), 47

TABLE 2. IMPACT OF SUPPORTING ELECTROLYTE ON PRODUCT FORMATION

ELECTROLYTE	RESULTS
NaBr	low product yield; high byproduct yield
NaOAc	no product found insulating material precipitated on the anode
HOAc/NaOAc (pH = 4.75)	no product found insulating material precipitated on the anode
KSCN	low product yield; high byproduct yield (uncharacterized orange ppt)
NaClO ₄	experiment in progress at time of report.
KBF ₄	solution resistance too high; electrolysis aborted
LiClO ₄	good product yield; low byproduct yield
TEABF ₄	good product yield; no detectable byproducts

Electrolysis Conditions:

divided cell (medium glass frit)

anode: Pt foil (1 cm² in area)

anolyte: 0.1 M 2-AN, 0.025 M diphenyldiselenide, 0.2 M electrolyte in methanol

cathode: carbon rod

catholyte: 0.2 M electrolyte in methanol

TABLE 3. SUMMARY OF RESULTS FOR ELECTROOXIDATION OF SELECTED ARYLMETHYL KETONES IN DIVIDED CELLS.

Arylmethyl ketone	Conditions	Applied Cell Voltage (V)	Current (mA)	Time (hr)	Yield
2-AN	0.1 M 2-AN 0.2 M LiClO ₄ 0.025 M (PhSe) ₂	25	30 - 8	4	65 %
2-AN	0.1 M 2-AN 0.2 M TEABF ₄ 0.025 M (PhSe) ₂	25	30 - 8	4	73 %
4-HAP	0.1 M 4-HAP 0.1 M p-TSA 0.2 M TEABF ₄ 0.025 M (PhSe) ₂	25	35 - 18	6.5	77 %
4-HAP	0.1 M 4-HAP 0.2 M TEABF ₄ 0.025 M (PhSe) ₂	30	40 - 7	6.5	25 %
4-MAP	0.1 M 4-MAP 0.2 M TEABF ₄ 0.025 M (PhSe) ₂	30	25 - 6	8.5	70 %

Note: Yields have been determined by integration of chromatographic peaks (mass selective detection).

Isolated yields are lower.

ELECTROSYNTHESIS OF 2-AN-ka

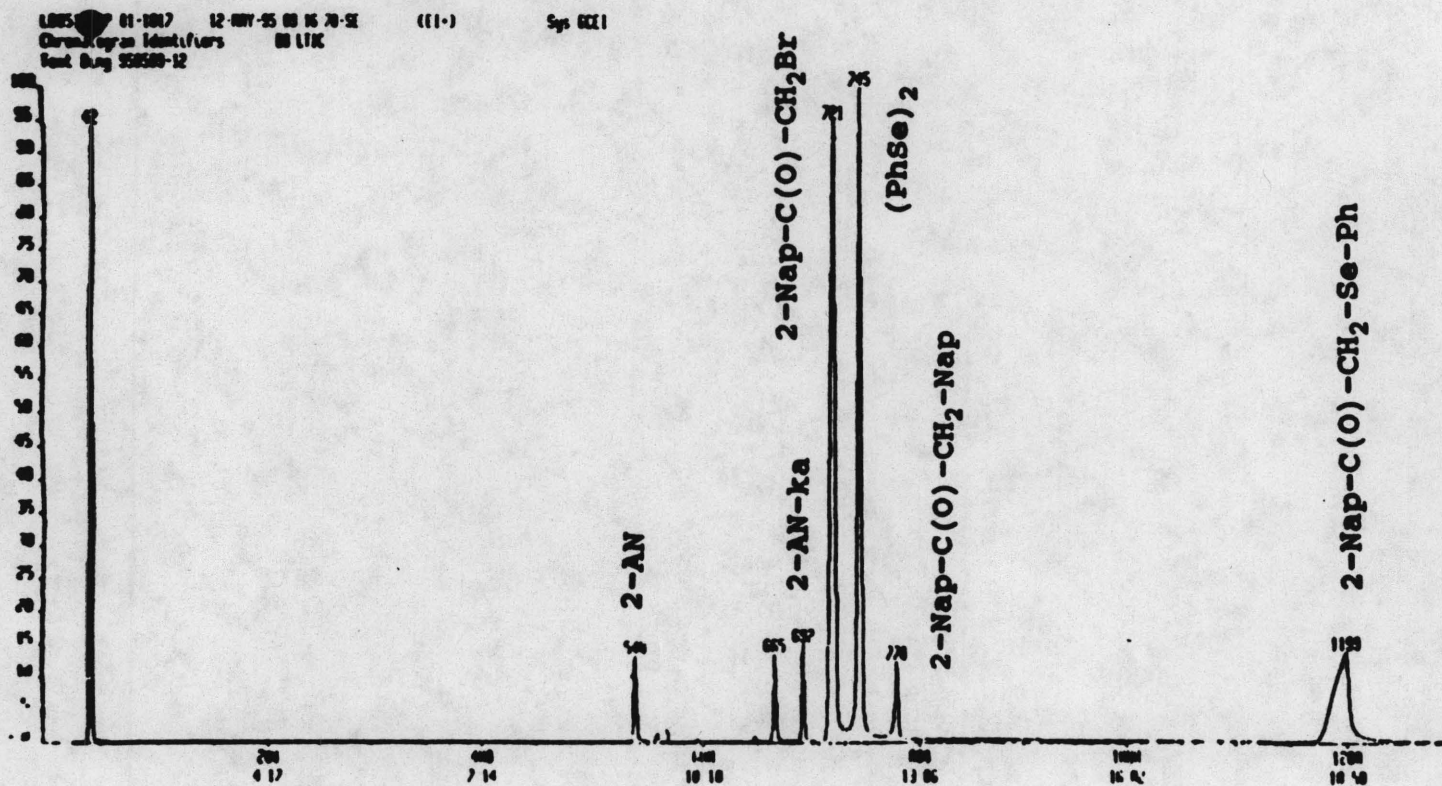
Conditions:

0.1 M 2-AN
0.2 M NaBr
0.05 M (PhSe)₂
0.1 M p-TSA

Voltage: 18.7 to 22 V
Applied Current: 30 mA
Electrolysis Time: 4.0 hrs
Divided Cell

Product Analysis:

2-AN-ka
2-AN
Ph₂Se
2-Nap-C(O)-CH₂(OMe)
2-Nap-C(O)-C(O)OMe
(PhSe)₂
2-Nap-C(OMe)₂-CH(OMe)₂
* 2-Nap-C(O)-CH₂Br
2-Nap-CO)-CH₂-Nap
2-Nap-C(O)-CH₂-Se-Ph



ELECTROSYNTHESIS OF 4-HAP-ka

Conditions:

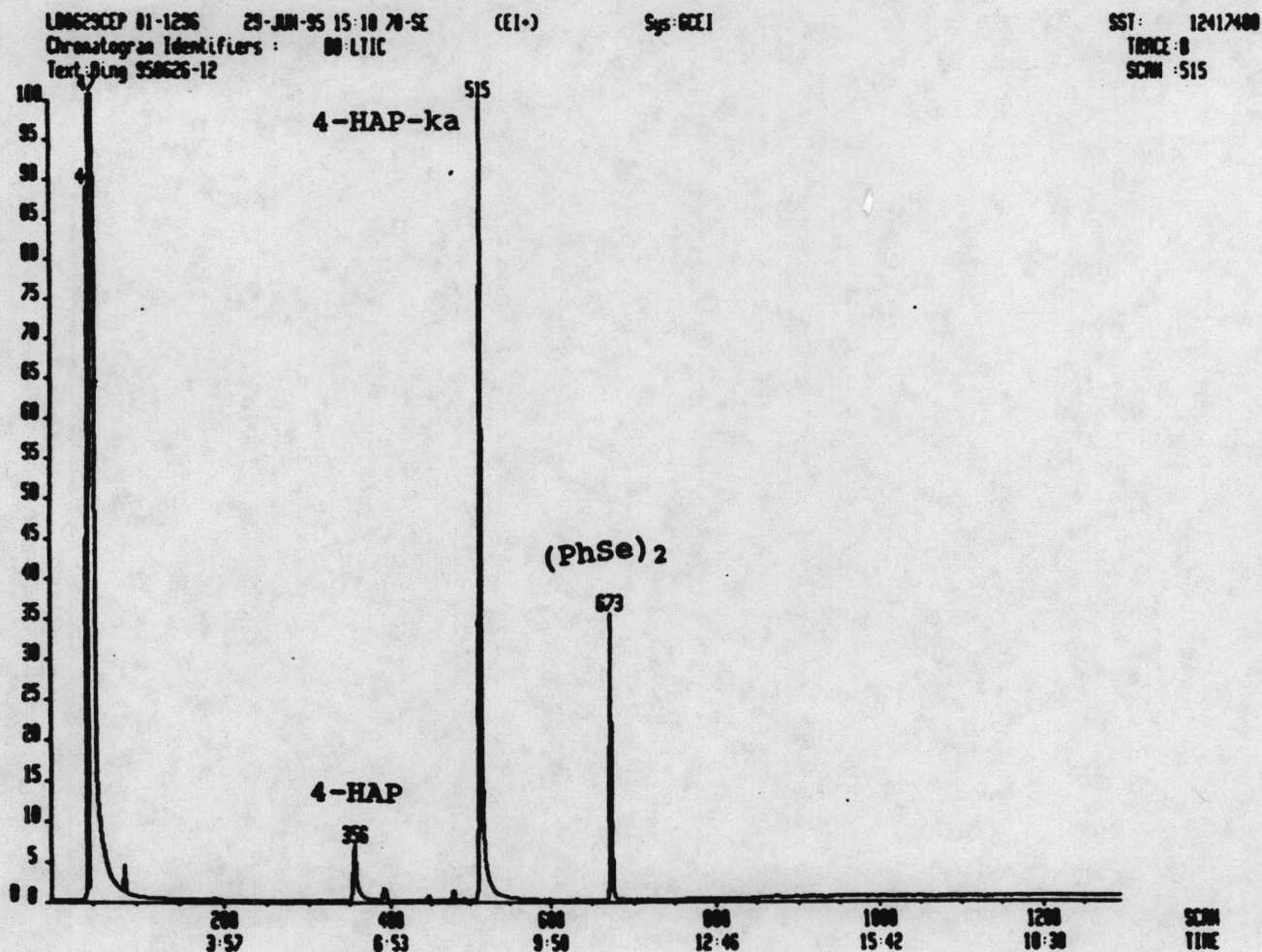
0.1 M 4-HAP
0.1 M p-TSA
0.2 M TEABF₄
0.025 M (PhSe)₂

Applied Voltage: 25 V
Current: 35 dropping to 18 mA
Electrolysis Time: 6.5 hrs
Divided Cell

Product Analysis:

4-HAP
4-HAP-ka
(PhSe)₂
plus 3 minor components (see chromatogram)

Yield = 77 %



ELECTROSYNTHESIS OF 4-MAP-ka

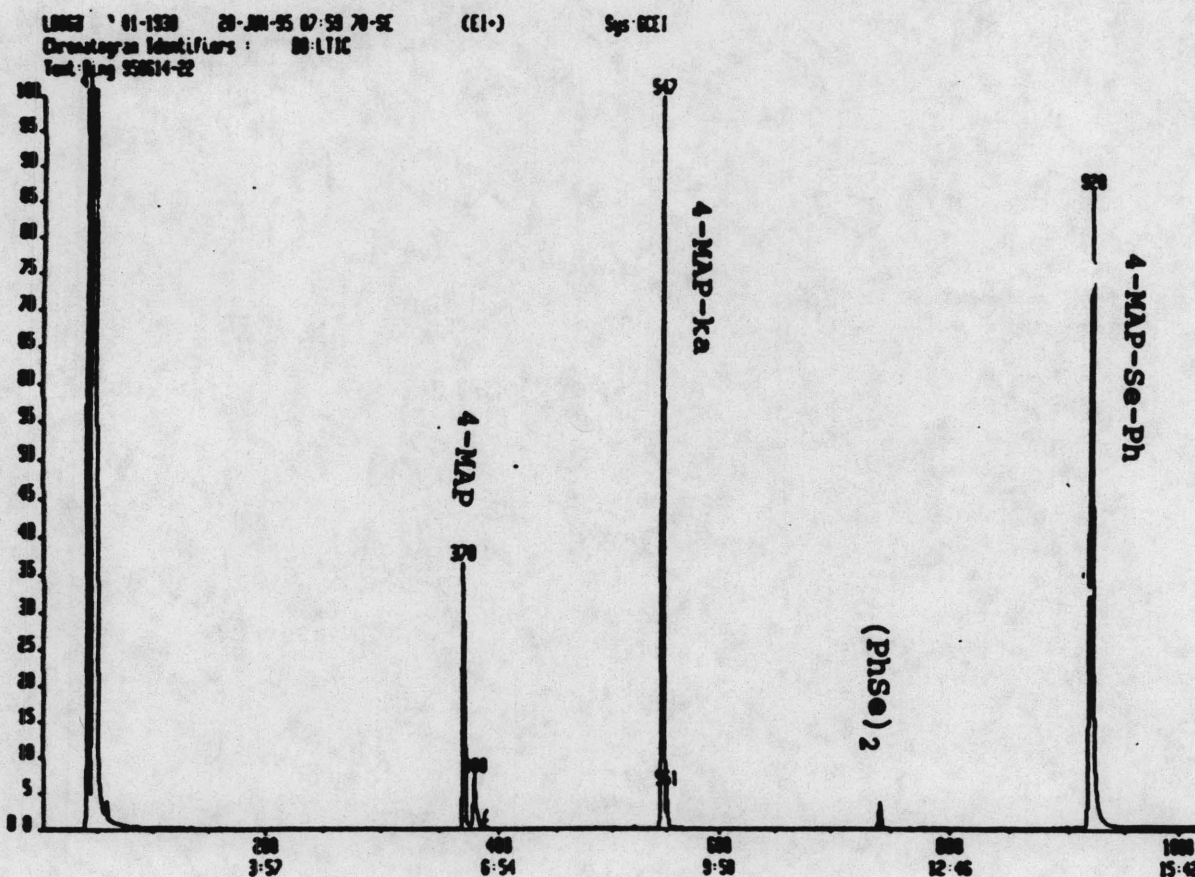
Conditions:

0.1 M 4-MAP
0.2 M LiClO₄
0.025 M (PhSe)₂

Applied Voltage: 20 V
Current: 23 dropping to 4 mA
Electrolysis Time: 8.0 hrs
Divided Cell

Product Analysis:

4-MAP-ka **Yield = 35 %**
4-MAP
(PhSe)₂
4-MAP-Se-Ph



ELECTROSYNTHESIS OF 4-MAP-ka

Conditions:

0.1 M 4-MAP
0.2 M TEABF₄
0.025 M (PhSe)₂

Applied Voltage: 30 V
Current: 25 dropping to 6 mA
Electrolysis Time: 8.5 hrs
Divided Cell

Product Analysis:

4-MAP-ka Yield = 70 %
4-MAP
(PhSe)₂
4-MAP-Se-Ph

