MILLIKEN RESEARCH CORPORATION

Spartanburg, South Carolina

LABORATORY NOTEBOOK

Name Kaye Sudeth Book No. 10004

Used from Ap 1996 To May 3, 1996

Laboratory Book No. 10004

Date Received: April 8, 1996

Assigned To: Kaye Suddeth

Returned To:

Date Returned:

This book is the property of Milliken Research Corporation. The Assignee is responsible for its return to the permanent records of Milliken Research Corporation.

NOTEBOOKS ARE NOT TO BE TAKEN OUTSIDE OF THE COMPANY OR CORPORATION PREMISES WITHOUT THE PERMISSION OF DIRECTOR OF RESEARCH.

The procedure outlined below is required for one purpose primarily---to make the notebook acceptable as indisputable legal proof in patent proceedings of what was done, and exactly when it was done. The exact date on which a given idea was first in mind has often been the basis for awarding valuable patents. Therefore, as soon as you have any idea, even though it may seem trivial or obvious to you, you will, under the procedure outlined, put it in your notebook with complete details. This will apply whether it is a small modification in experimental procedure or apparatus design which may give improved yields or operation, or what may be a major improvement or innovation in products or processes. **GET IT DOWN.**

The early date of record may mean the difference between getting an important patent for the Research Corporation in your name, or losing it to some other company which can actually keep our stockholder mills from using the idea.

If after further thought and discussion, or a few experiments, you decide that the idea may have value, you may draw up a formal description, either as a memo or on the invention record form provided, for submission to the Patent Division.

It is a function of the Patent Division to review the yellow sheets in this notebook as forwarded by you and to cull from them all ideas having patentable novelty, but the invention record form submitted in this way will serve to accent those ideas considered by you to be most important.

PROCEDURE FOR
KEEPING LABORATORY NOTEBOOKS

1. Make all entries in ink and as legible and complete as possible.
2. Every pair of sheets is consecutively numbered, and all entries should be made on the white sheets with a carbon paper between the white sheet and the next succeeding yellow sheet. The yellow sheets, which are perforated for easy removal, are torn out daily and forwarded to the administrative office of the Research Corporation. No white pages (containing the original of the entry) should be torn out under any circumstances.
3. All experimental data is to be entered in this book, and as far as possible, all calculations, graphs, drawings and notes of any character should be entered herein. When patents are referred to, include patent number. When literature is referred to, include complete journal references (Author, Volume, Page, Date).
4. Make all entries in this notebook **first.** It is extremely important that this notebook be what the law calls a "notebook of original entry." Make your first notes about anything—weight, temperature, time, ideas for future work, drawings, sketches—**in this notebook.** If you want to keep a separate tabulation in special cases, do your transcribing of data from the notebook into the tabulation, but not the other way.
5. When starting a problem use the following heading:

   Subject:_____Project No._____

   Experiment No._____Test No._____

   If work done on the problem for the day fills more than one page, continue on next page and start heading:

   Project No._____Continued

   If work done on the problem for the day fills part of page, use the remainder of page for the next problem worked on that day and fill in the complete heading. Make all your entries in strict chronological order. If you are working on several experiments at once and making alternate observations, use the full heading at the start of each experiment each day, and for later entries on that day you need only note the experiment number beside the data.
   Date and sign every page or after each problem on the same page.
   The full date should be entered, e.g., July 1, 1946, not 7/1/46.

   Do not leave blank spaces after experiments. If there is only a small amount of space, 1 to 2 inches, left at the end of the page when an experiment is finished, draw diagonal lines through this space.
   Have an associate, if possible a superior, witness the record of the entire experiment and the signature of each experiment. He should be someone qualified to understand the record.
6. Erasures should never be made. Draw a line through the incorrect work or entry. Never make corrections on a page after signing and dating. If it is at any time observed that a cancellation or addition should have appeared in an earlier entry, a new entry should be made, stating what should be cancelled and what addition should have appeared in the earlier entry.
7. When an experiment must be started on one day and completed some days or a week later, space should not be left at the first entry for subsequent results, but when the results are finally received, the data from the original day's work may (but need not) be brought forward (with suitable reference to the page where they first occur) and the whole experiment summarized on the day on which the final data are obtained.
8. **Do your thinking in the notebook.** Whenever you have an idea of any kind on future experimental work, whether it bears on your own problems or those of other laboratory or research sections or of others with whom you may be engaged during the course of your work, jot it down in your notebook at once, with as much detail as possible. Do the same for proposed apparatus layouts and experimental procedures.
   After any discussion, formal or informal, that bears on the work of the Research Corporation or other organizations engaging the services of Research Corporation, note what it was about and who was present. If you watch someone else carry out an experiment, make a note of what you saw and who was there.
   In short, make this notebook a diary so that anyone can go back to it years later (five to ten years is not unusual in patent actions) and report without question what you did, what you saw, what you thought, who was present, whom you spoke to, what you discussed and **when all this occurred.**
9. Index experiments on index pages in front of book.
10. When describing experimental work in weekly or monthly reports, always include the notebook and page numbers on which the work can be found.
11. When a book is filled, it is checked and approved by your section or division head and returned to the Patent Division for filing, unless it is to be retained for reference. However, only one finished book may be retained, and all other finished books must be returned to the Patent Division unless specific permission for their retention is obtained from the Director of Research. If other notebooks are later needed for reference, they can be charged out.

INDEX

unless otherwise indicated in specific outlines the following equipment/instrumentation is used for all work.

Hood R082 (lab 62)

Top load ~~balance~~ balance 1041/5/4 - 00041
analytical balance - 00038
Agilent - 00178
HPLC - 00049
spectrophotometer - 00182
Solvent microwave - 00222 (freezer)
solvent oven (constant temp) - 00200
pH meter - 00505
IR - 00014
GC - 00089

Frequently used DV methods may be referred to as follows.

DV1 - oven solvent
DV300 - % solvent (microwave)
DV13 - % H_2O by Agilent (in moisture)
DV5 - pH (straight, unless otherwise indicated.)

DV383 - refers to a cyclo valve method where an initial sample is weighed into a loose flask (volumetric) & diluted to the mark c̄ a specified solvent. Then a stated volume is transferred to a 2nd loose flask & diluted to the mark with the same solvent. Calculation:
$\frac{\text{absorbance}}{\text{sample wt}} \times \text{pipet volume} = CV$

DV5TC - Sometimes referred to a "internal standard". Initial sample is weighed into a 100 ml volumetric flask & diluted to the mark with a specified solvent. Then a specified amount (usually 10ml) is transferred to a 1 litre volumetric flask & diluted to the mark c̄ solvent

Cont.

INDEX

DV 389 - Refer to PMA or phosphomolybdic acid test.

~~DI~~ I Headspace test - (To my knowledge, there is not a DV for this). Hold a moistened piece of KF stained paper in ~~the~~ headspace of a RXN for ~15 seconds. Monitor the paper for instantaneous formation of a blue/black color. The development of this color indicates the presence of even minute.

A ~~abbreviation~~ used - $\bar{S}$ = without
$\bar{C}$ = with
$\therefore$ = therefore.

INDEX

Attempt to make an amino using Cyanuric acid + 10063-61 (can epoxide from methyl carbitol + epi) using in KOH catalyst - 1, 2, 5, 9,

10063-72 cont from 10063-72 - 3, 4, 14,

10063-75 cont from 10063-75 - 6, 7, 8,

Attempt to make epoxide from methyl carbitol SE015PO + epichlorohydrin using stannic chloride catalyst - 10, 11, 15, 17, 18,

Attempt to make epoxide using methyl carbitol + epi + stannic chloride catalyst - 12, 13, 16, 19,

Attempt to make epoxide using methyl carbitol epichlorohydrin + stannic chloride c̄ NaOH, ~~at higher temp & less t~~ KSH/KOH c̄ less NaOH, 20, 22, 24, 25, 26, 27,

Attempt to epoxidize methyl carbitol SE015PO + epi + stannic chloride using ↓ NaOH - 21, 23, 28, 29, 30, 31, 32,

Dimine + epoxide c̄ KOH catalyst - 33, 34, 37, 40, 45

Dimide + epoxide c̄ KOH catalyst - 35, 36, 38, 39, 41, 42, 43, 44

INDEX

Cyan using amine derived amine (1000433) – 46, 47, 48, 49, 51, 53, 61

Cyan derivative made from SEO amine derived amine & PEG400 MF as solvent – 50, 52, 54, 57, 1054/24/4c, 64

Cyan derivative made using a hydrogenated ~~benzy~~ 1054/24/4c benzylamine – 55, 56, 58, 59, 60, 62, 63, 68

2-hydroxyethylphthalimide made from monoethanolamine & phthalic anhydride – 65, 66, 67

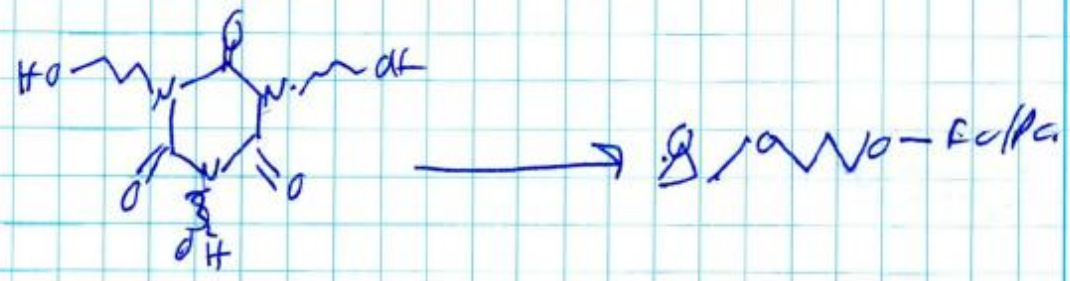
Alkylated amine derived from imide treated c 1 Colt. – 69, 71, 75

alkylated amine derived from an imide + BGE c BF_3 catalyst – 70, 72, 74

Alkylated amine from imine by deprotection c hydrazine hydrate – 73

✓ ~~Contract~~ entered on Colum inter Index

Objective - React 10063-61 with cyanuric acid using KOH as catalyst.



Procedure

1) Equip a 250 ml RB flask w/ stirrer, condenser & heating & N2.

Stirrer + flask = 306.3g

2) Charge 13.0g (at 100%) of 1,3,5 tris (2-hydroxyethyl) cyanuric acid. Added but it is 97% pure ∴ used 13.4g. mw = 261.24 = 0.05 mole

3) Charge 28.4g of 10063-61. mw = 189, = 0.15 mole. & only have 24.2g = 0.13 mole

4) Stir ~5 minutes w/ N2 sweep.

5) Charge 0.5g of KOH pellets stir 5 minutes. The cyanuric acid is not in solution at beginning of heat up.

6) Slowly heat to 130°C.
- 1st step heat to ~80°C, lengthen to 96°C. Still not in solution. Hold 5 minutes at this step.

Date April 5, 1996 Signature Kaye E Sudbeck

Date April 14, 1996 Witness Bruce Sudbeck

Cont page 2

10004-1 cont.

Heat on wh. water bath reaches ~118-120°C it exotherms violently. My thermometer goes to 150°C & the reading rises much above 150°C

7) Cool bath down. Save the bitty mixture because has light yellow. after exotherm. All the cyanuric acid seems to be in solution

8) Heat bath to 130°C for E2.
No exotherm this time.
On temp 12:15pm

9) 2:15 pm sample for GC.
60°C for 2 min, ramp at 10°C/min to 300°C, hold 5 min at 300°C.
SP 2/CC, glass NCC.

put ~3 drops reaction mix in 5 ml reagent methanol - 7 ml injection.
No peak (except solvent) seen. In order of a sample ~5 times were concentrated & re-run to be sure.
See many small peaks - one at 10.62" - epoxide
one at 12.83 - alcohol, large peak at 23.56"
& no large peak in addition of concentration, no dimer due to underlayer of epoxide?
Part 1 Crow.

Cool & seal

cont. page 5

Date April 8, 1996 Signature Kaye E. Swedlett
Date April 14, 1996 Witness Brian Swedlett

10063-72 cont from 10063-73

Clear caustic over ~ 3 minutes, still see approx 10cc extra

11) Seal & heat to reflux for ~ 2 hours
On temp 2:25 pm - for 103°C.

Stop at 4:30 pm

Cool & Seal

Cont. page 7

Date April 8, 1996 Signature Kenneth E Swedler

Date April 14, 1996 Witness Bruce Ambeth

10063-72 cont for 10004-3

12) Charge ~~250 ml~~ 50 ml 165 g chloroform
Before chloroform NaCl mix i flask, top dark brown, bottom lt brown)
13) Phase
Became very cloudy i addition of chloroform
Ok formed 8:45 AM.
10:30 AM phase -
Bottom $CHCl_3$ - dark red brown slt vison
96.3g

Top - Med / light tan, cloudy.

Drain bottom ($CHCl_3$ product) into a 1 neck
500 ml RBF wt of flask - 165.9g
~~96g dry~~ 165 g/cd 9s

(14) Add another 50 ml chloroform to
H_2O layer & extract organic -
begin 10:45 AM.
end 12:20

Top - H_2O - Med red brown
- 185.3g

Bottom - $CHCl_3$ / product light golden brown / hazy
- 60.7g

Drain bottom into 1 neck flask from step #13
15) Strip - only 18 ml of ~~CHCl~~ $CHCl_3$/d 9s
distillate recovered for dryers
flask + stopper Sample = 188.6g - 22.7g product

Date April 10, 1996 Signature Gary L. Sudetts
Date April 14, 1996 Witness Bruce Sudetts
Cont pg 14

10004-1 cont for 10004-2.

10) Remove ~2g for analytical purposes

(11) charge 100ml H_2O

12) Slowly charge 15g 50% NaOH.
(Denver D4723)
Charge over ~15 minutes ~40°C exotherm

13) Heat to ~~[illegible]~~ 95.8°C 4/10/96 reflux for ~2 hours
on ~~temp~~ ~~10:30~~

Cool & seal

cont

Date April 10, 1996 Signature [illegible]

Date April 14, 1996 Witness [illegible]

10063-75 cont from 10063-75.

10) Per EZ - Filter through #4 paper into a Buchner.

11) Run DV-TI "Determination of F-Poxy equivalent weight".

a) methylene chloride & glacial acetic acid solution: 163g of methylene chloride + 216g of glacial acetic acid (Aldrich 02624HN)

b) Prepare TBAI (tetrabutylammonium iodide) in acetone solution.
TBAI (Aldrich lot # 06703BG) 10g
+ 100g acetone (tech. grade)

GP put 70ml of methylene chloride/acetic solution in a beaker c̄ magnetic stir bar. Add 3 drops crystal violet solution. Titrate c̄ ~.1N perch to green endpoint. Turn yellow c̄ ~1 drop. When I read the method very closely I see it is set up for an autotitrator. The very small amounts. Don't know if an getting yellow exept through Per EZ do not wrong about the solvent. TBAI titrates first titrate filtered sample. Titrate 2 drops

a) - 2 step method - Sm = 0.7229g
add 70ml HHC(3)/acetic acid & 8 drops Crystal violet. Titrate c̄ 0.1016N perch (Aldrich 14604HN)

Date April 10, 1996 Signature [illegible]
Date April 14, 1996 Witness [illegible]

Cont page 7

~~10006~~ 1CS4/10/E5 10063-75 cont from 10004-6

Get green endpt but not stable after ~1.2ml
after 2.3ml seem stable

bb) add 10ml of TBAI/acetone solution (give bond to purple), titrate to green endpoint. Total 0.1016N perch used = 5.44ml.

$$\frac{(100\%\ \text{solids}) \times 0.7229\text{g sw} \times 10}{5.44\text{ml} \times 0.1016\text{N}} = \frac{722.9}{0.552704} = \underline{1308}$$

~~expected ~800~~ 1CS4/10/E5C expected 698 (per F2)

cc) Now do one-step method.
sw = 0.7720g & used 8.76ml of 0.1016N perch.

$$= \frac{10(\%\ \text{solids}) \times 0.7720 \times 10}{8.76 \times 0.1016} = \frac{772}{0.890016} = \underline{867.4}$$

dd) Now do a 3rd method. (ASTM method D1652-90) (method B)
sw range = ~~600-1000~~ 1CS4/10/E5 0.7-0.8g
actual sw = 0.8410g

- Add 10-15ml CH_2Cl_3 to specimen. Stir. Used 11ml
- Add 10ml of TBAI solution
- Add 6-8 drops of crystal violet (same as above: = 0.1g crystal violet in 100ml acetic acid)
- Titrate 9.6 8ml of 0.1016N perch

Cont page 8

Date April 10, 1996 Signature George E. Sweller
Date April 14, 1996 Witness Bruce Gadsleth

10663-75 cont. for 10004-7

1st calculation = $\frac{4.3 \times 9.68\,ml \times 0.104\,N}{0.8410\,g}$

$= \frac{4.2289984}{.8410} = 5.0285$ eq. wt Eo

$WEEW = \frac{43 \times 104}{5.0285} = \underline{855.1}$

Per E2, the ~850 # is solvent correct. We believe the # is due to problem reported in DV I #425 (review 1/86) pg 3 of 5 Troubleshooting slip #4)
– actual lower price #404 for above titration

12) Now (DV 12) run a fine #.
SW = 4.9532 g odd ~ 10 drops phenolphthalein did not turn pink.
Wait time = ~~[illegible]~~ 10 S
weigh ~ different sample.
0.5224 g used ~ 0.2 ml of 0.5N KOH (turned pink)

acid # = 0.98 acid #

If we adjust Epoxy equivalent wt for acid #, the EEW ≈ 846 (stick ↑) for info to E2. Transfer sample to labeled jar.

Date April 19, 1986
Date April 14, 1986

Signature Kenneth Swoden
Witness Bruce Gaddett

10004-1 cont for 10004-5.

14) Charge 50 ml chloroform & ~~pt~~ 1 CCS yields
Before charge RXN is clear, pale ~~green~~ yellow
15) ~~Start~~.
Begin 8:20 AM
3 pm — top (H_2O) is pale yellow green
bottom ($CHCl_3$/product) clear, almost colorless

16) Drain bottom ($CHCl_3$/product) into a 500 ml Erlen. wt of flask = 156.6g
80.0g of product/CH_3Cl_3 drained.

17) Charge can add back 50 ml $CHCl_3$ to H_2O layer. Stir ~1 hour

18) Top H_2O pale yellow clear
Bottom - clear, almost colorless

19) Collect product in same Erlen as step #16.

20) Strip. / collect 38g $CHCl_3$ for disposal
flask + stripped product = 167.7g = 11.1g product
21) Chal DUB (5 H_2O) a product which is clear, slt viscous, pale yellow/green liquid. SW1 = 0.0970g / = 0.2638 / AVG = 0.2478
SW2 = 0.0963g = 0.2319

Conclusion - product to EL for evaluation

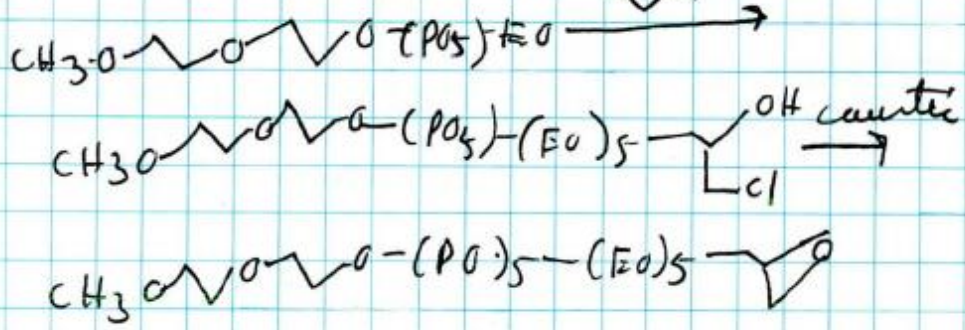
Date April 11, 1996
Date April 14, 1996

Signature Kaye E. Sudduth
Witness Brian Sudduth

Objective - ~~React an amine (9990-73)~~ IC 54/11/86

React Methyl carbitol 5PO/5EO (9990-73) OH# 90.2 with epichlorohydrin using stannic chloride catalyst. Run at 50°C, post cook at 70°C. (Kluge method).

Procedure -



1) Equip a 2 litre RBF c̄ thermometer, stirrer, condenser, heating & N_2.

flask + stir assembly = 753.3g

2) Charge 373.2g of 9990-73 (clear golden yellow liquid) mw 621.9 = .66 moles

3) Start agitation, N_2 sweep

4) Dropwise, charge 3g of stannic chloride (AKA - Tin IV chloride) mw = 260. Aldrich # 03429MX No exotherm, slight thickening, Balance # 00187

5) Heat to 50°C, slowly

6) Slowly dropwise charge 66.6g *epichlorohydrin (mw = 92.5 = 0.72 moles) over hour @ 50°C. Balance 00187

Begin - 10:55 AM (MXL air) ; yellow cloudy temp = 46.2°C
11:10 temp = 46.5 *(Dow Chem # 1262276)

Date April 11, 1996 Signature Faye E Sutton

Date April 14, 1996 Witness Bruce Sudeth

Cont page 11

10004-1C cont

-11:55 temp = 45.4°C RXN mix is red brown / cloudy
no real exotherm seen yet.

12:20pm temp = 47.5°C.
12:35pm heat - 47.5°C
Complete 12:40 pm - 47.4°C

2) Stir not 5 minutes (include at lunch)

3) Heat to 68-72°C.
begin heat up 1:50pm.
on temp. 2:15pm
No problem c̄ exotherm
5:30pm RXN pale brown, hazy. temp = 68.9°C.

EZ to stop heat / condensation at
~7pm.

Cont page 15

Date April 11, 1996 Signature Kenneth E Szeszler
Date April 14, 1996 Witness Brian Sudlett

Objective: Try to epoxidize methyl carbitol using epichlorohydrin with a stannic chloride catalyst

Procedure:

1) Equip a 2 liter 3 neck r round bottom, stirrer, nitrogen inlet & heat

2) Charge 120g methyl carbitol (mw = 120 - 1 mole) Density lot # M0144. Agitate & sweep w/ N_2

3) Charge 2g stannic chloride (Aldrich # 03429MX) use balance # 00187. Smoke very much after charging.

4) Heat to 50°C. * Exotherm at ~48°C give to 62°C. Cool & heat again - exotherm again. Turn down heat setting - Finally stabilizes

5) At 11:20 AM begin adding 111g of epichlorohydrin (Aldrich lot # 13622TG). Use temp of 80°C on Balance 00187
11:20 AM - temp = 46.9°C, clear about color of rxn
12:10 pm - temp = 50.5. mod exotherm but not bad.
12:35 pm - temp = 50.1°C, color, hazy.
complete 2:40 pm - temp = 52.4°C

6) Stop stirrer

7) Heat to 68-72°C, on temp 2:45 pm
color, slightly cloudy.

Date April 11, 1996 Signature Faye C Sandbeck

Date April 14, 1996 Witness Bruce Sandbeck

cont pg 13

10004-12 cont.

Refer show no [illegible]
5:20 pm - [illegible] slt cloudy.
E 2 to cut heat at ~ 7pm
Leave for lein.

cont page 16

Date April 11, 1996 Signature Kaye E Sutter
Date April 14, 1996 Witness [illegible]

10063-72 cont for 10004-4

16) Filter through #4 paper in a Buchner funnel.

17) Check DV 13 (Σ H,C)
SW1 = 0.0705g = 0.4559%
SW2 = 0.1547g = 0.4229%

~~15) Check energy equivalent with using ASTM method D1620-90, method B. Using per E2, no epoxide at this pt. should be an amino.~~

18) Run GC,
<u>conditions</u> 60°C for 2 min, ramp at 10°C/min to 300°C. Hold 5 min.
SP2100, glass NOC.
sample wt. 0.5g in 5 ml reagent methanol
4 ml injection.
multiple small peaks. I do not know what I am looking for. Leave for E2 to interpret.

Date April 11, 1996 Signature Karen E Siedell
Date April 14, 1996 Witness Bruce Andreth

10004-10 cont from pg 11

9) Run mix pole from, slt viscous
charge 16 ml FPA at room temp.

10) Prepare a solution of 100 ml H_2O of
$57.6g$ of 50% NaOH. Charge dropwise
do not exceed 35°C.
Cont - Begin at 8:30
Complete 9:30 AM

11) Heat to 70°C.
On temp 10 AM (Hold ~5 hours)
pull ~~JC~~ sample after ~2 hour 1/S 4/1/99
~~12:05 pull JC sample, run on clave,~~
~~Cool Inject~~ 1/S 4/1/99 run sample
Hold at temp 5 hrs
D. forgot to pull 2 hr sample equivalent
sample

12) 3pm. Pull 10g sample. Add 20 ml $CHCl_3$ to
~5% the Phase. Pour phase
agent HCl/water 1:2 ~ 20 ml H.C.
2nd phase - good - Top clear bottom (hazy)
3rd phase - fair
Stop

Continue heating RXN mix.

fire to other vessel, pour
not off to complete equivalent
equivalent today

Cool RXN's & seal with marker
Cut ~~today~~ 1/S 4/1/99 but 4:45p

Date April 12, 1996 Signature Kenneth E Switzer
Date April 14, 1996 Witness Brian Hollett

Cont pg 17

10004-12 cont from p 13

8) Rxn mix is then, slt cloudy c slt pink tint.

9) Pull GC sample (0.5 ml in 5 ml methanol) and injection: 60°C for 2 min, 10°/min to 300°C hold 5 min on SP2100 after NOC. ~~[illegible]~~ See results below.

10) Evaporate 27 ml IPA

11) Pour reaction solution 200 ml H_2O / 96g 50% caustic (Barney Jet #4130). Transfer to an addition funnel & add dropwise, hold temp < 35°C
Begin 8:40AM Complete 10:45AM

* GC results:
peak at 4.796" - area - 99.8 - ethanol then in cabitol
peak at 10.731" - area - 93.2 - greasy
peak at 13.70" - area - 537.9 - allethylidrin
peak at 19.06" - area - 743.5 diene
while caustic going in, short carbitol at the gradient, some peak an above carbitol. Also peak at 6.57", very large. ie retention shift due to peak size?

12) Heat to 70°C overnight 1:20AM
~~[illegible]~~ 1:20 pm pull sample for GC
an above
small peak, 4.87" - carbitol, area = 29.5207
smaller peak, 12.87" - area - 22.67
peak at 14.13" - ? area - 185.5113
peak at 23.73" area - 69.6779
Ed says he expects yield 84 to be state of allethylidrin
4:45 pm cut heat & seal into tubes

Date April 12, 1996 Signature Gary E. Swartz
Date April 14, 1996 Witness Brian Middleton

Cont pg 19

10004-10 cont from pg 15.

13) Take the small stoppered object & determine epoxy equivalent wt using ASTM method D1652-90 sections 16 & 17.2.
expect EEW around 690. eq/kg, of unknown KS4118 using Tetrabutylammonium iodide. instead of Tetraethylammonium Bromide as called for in the method. Should be okay per Prof Van Pohn, but notify EZ.

Run the sample as before for you until we resolve the bromide vs. iodide question.

sub = 0.7942 g
charge 10.5 ml $CHCl_3$
charge 10 ml TDAI / acetone solution
charge & dissolve optional water in acetic acid
Titrate c 0.1016 N Perchloric acid (Aldrich lot 14604KN)

Use 10 ml pipet #404. Note this pipet was filled this morning & will be applied at the end of the day. It will not stand c acid for extended period

I used 2.8 ml of 0.1016 N perch.

$$\frac{4.3 \times 2.8\,ml \times 0.1016}{.7942\ g} = 1.5402$$

$$WEEW = \frac{43 \times 100}{1.5402} = 2791.8\ ?$$ very high.
Not the 4 expected strange DG search

Cont pg 18

Date April 15, 1996 Signature Kay E. Sutcliffe
Date April 16, 1996 Witness Rick Reb

10004-10 cont from p 17

repeat, eew

SW2 = 0.8306 wet 2.5 ml (?)

$$E = \frac{4.3 \times 2.5 \times .1016}{.8306} = 1.3150$$

$$W_{eew} = \frac{4.3 \times 106}{1.3150} = 3269.8$$

Porcelain - E2 believes the Rxn potential in decomposition of NaOH. This theory is supported by what we see in 10004-12 (model compound) above.

The mineral is gold, & clear & silky visom

Keep a labeled vial of dry of remainder in ethylated waste

Date April 15, 1996

Date April 16, 1996

Signature Kayne Sadler

Witness Rick Reb

10004-12 cont. from p 16

13) Start from small HC sample, same prep'd condition as before.
Sample show lots of peak at ~14" & small peak at 23" & 25".
No peak at ~19" as expected.
EZ fraction is low decomposed
But, on a $CHCl_3$ wash & then
start another HC
Start c ~10g sample. wash $CHCl_3$ c
HC x3. Start. $CHCl_3$ large - 7ml
While this HC sample is running,
go ahead & strip the aliquot

Submit some of the stripped aliquot
for HC-MS.

The HC in $CHCl_3$ show a
power peak at 4.816" - expected
slightly smaller peak at 12.96" -
peak about 1/2 of previous at 17.45"
small peak at 21.744 & 26.51"
(see attached). Material is clear, pale yellow supernatant

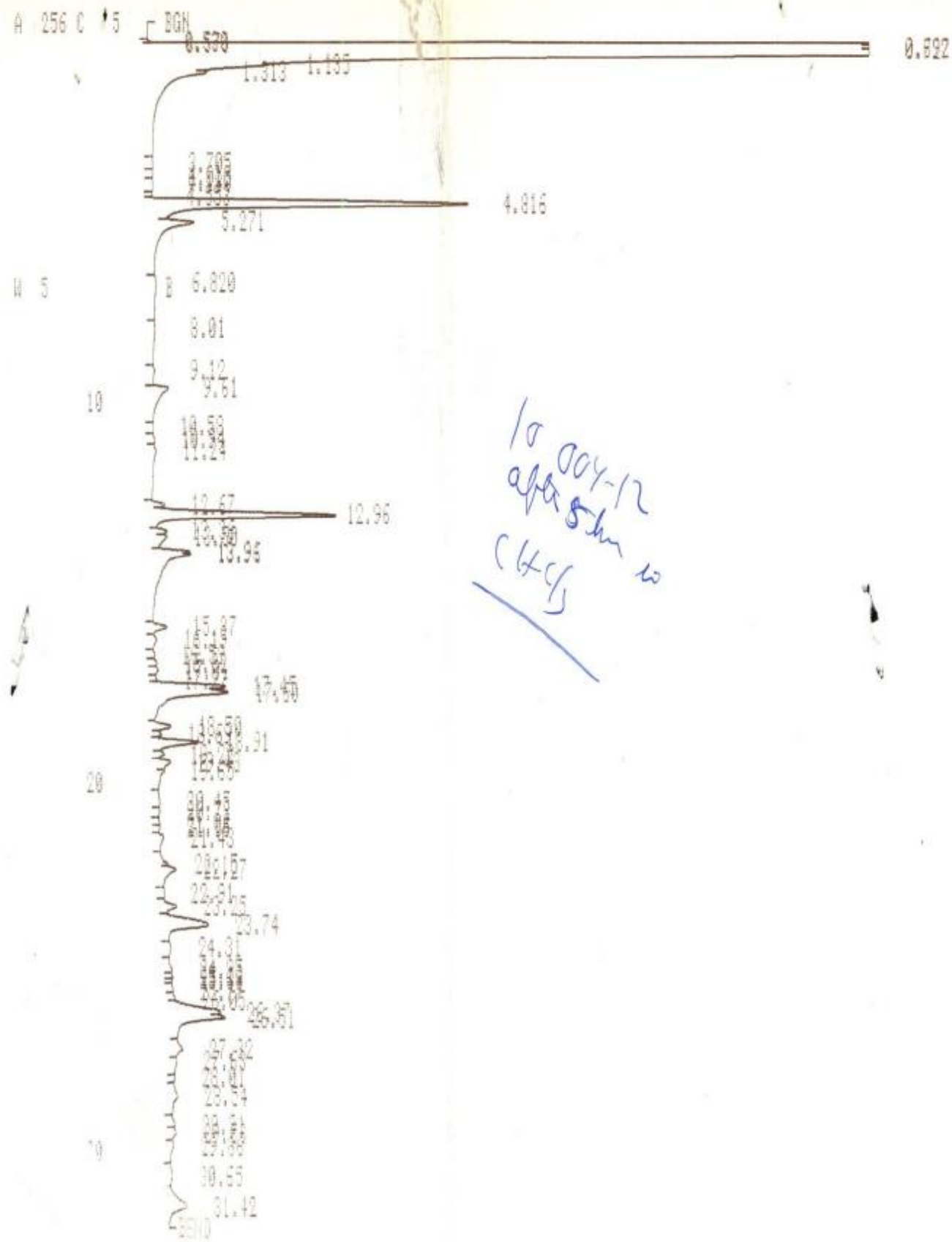
Conclusion
Re EZ, reaction is decomposing, probably
due to oxygen content.

Key is find return & figure of the reaction
attempted under

Date April 15, 1996
Date April 16, 1996

Signature Kuyu E Jeffrey
Witness [illegible]

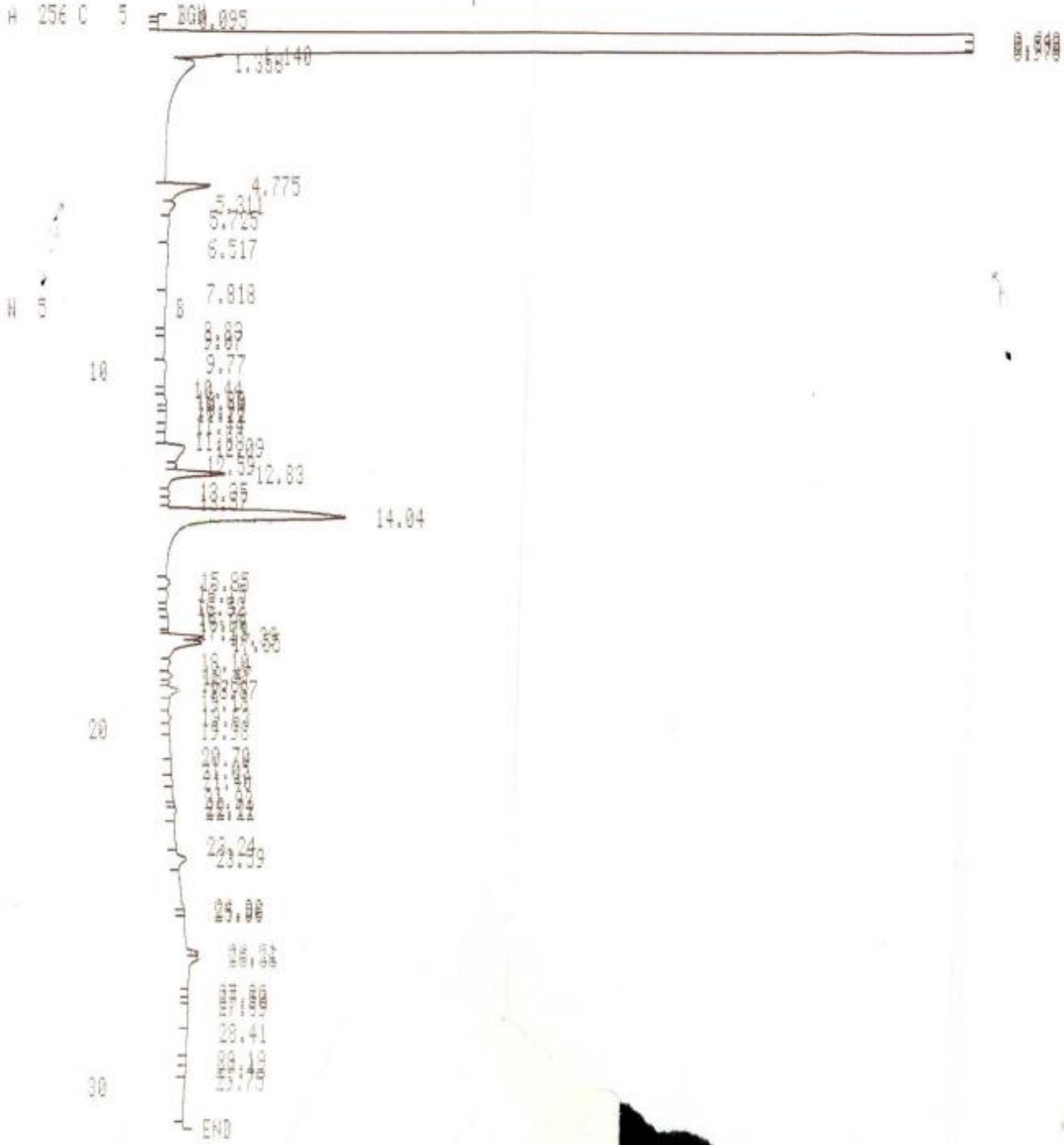
METHOD CURRENT



10 004-12 5h 260 end

RUN 2 19:40 96/04/13

METHOD CURRENT



RUN 3 20:19 96/04/

Objective - Repeat 10004-12 except use less NaOH & do the NaOH step at room temp.

Procedure -

1) Equip a 2 liter 3 neck c̄ thermometer, stirrer, N_2 heater & cooling.

· wt of flask + stirrer = 783.3g

2) Charge 120g (1.0 mole) methyl carbitol (Dow, M0144)

3) Begin agitation, N_2 sweep & condenser.

4) Charge 2g of stannic chloride Aldrich 03429MX
Smoker, and premix ~4°C exotherm

5) Heat to 80°C. solution

6) Charge 111.6g epichlorohydrin (mw = 92.5 = 1.2 mole)
Aldrich 12622TC. Hold temp < 80°C. setpt = 46.0°C
~~Begin 2 pm temp = 48.3°C~~
2:16 pm -- ~~temp~~ = 48.1°C
2:40 pm - temp = 49.1°C
3:15 pm - temp = 52.4°C - ~40ml left.
3:28 pm - temp = 53.5 - 1
* Batch this mixture & 10004-21 seem went together during heat up.
4:05 pm = temp = 55.6 complete
next temp = 55.7°C

7) Heat to 65-72°C. on temp 4:25 pm
cut heat & seal c̄ N_2 blanket 5:40 pm
on temp 55 for 1 hr, 15 min

Date April 15, 1996 Signature Kenneth Swartz
Date April 16, 1996 Witness [illegible]
Lent pge 221

Objective - Report 10004-10 except use less NaOH, & do the NaOH step at room temp.

Procedure -

1) Equip a 2 litre 3 neck r.b. thermometer, stirrer, N_2, condenser & heating, flask + stir assembly - 8 21.8g

2) Charge ~~373.25~~ 336.0g ICS 4/18/96 9990-73 methyl carbitol + 5 PO + 5 EO, pale yellow, slightly cloudy material. + ~~0.6 moles~~ ICS 4/18/96 0.54 mole

3) Begin agitation, condensation & N_2 sweep

4) Charge 2.7g stannic chloride (Aldrich 03429MJ) bottle sense pressure, mild smoking, ~20°C exotherm

5) Heat to 45-48°C & slowly, temp.

6) Charge 59.95 g epichlorohydrin (volume 00187) Aldrich lot # 12622TG (mw = 92.5) Bath Temp ≤ 80°C → sat pt - 46.0°C

Begin 2 pm temp = 45.0°C
2:10 pm temp = 49.2°C
2:40 pm - temp = 51.3°C
3:15 pm temp = 52.8°C
3:20 temp = 51.7°C

about 5 mo left. complete. max temp = 53.2°C

7) Hold at ~~48-52°C~~ 68-72°C for 4 hours begin 8:35 pm

Cut heat 5:35 pm on temp 2 hours so far
Seal to N_2 blanket

Date April 15, 1996 Signature Kenneth Snyder
Date April 16, 1996 Witness Rick Ritz

Cont. page 23

10004-20 Cont from pg 20

8) Heat again to N2 & condensation on temp 8:20 pm. Sample for GC after 1 hour. (Note: EX2 run a GC last night that showed RX, near completion, small amount of carbitol, small amount of epoxide, large amount of mono-chlorohydrin & small amount of diol).

GC condition:
60°C for 2 min, ramp at 10°C/min to 300°C hold 5 min. SP2100 glass, NOC column, Perkin Elmer 8500 GC, glass, NOC

Sample prep ~0.5g/5ml methanol, 5ul injection.

9:25A run pull sample

peak at 9.984" carbitol - area = 135.97
" " 10.952" ? area = 71.33
" " 14.220" chlorohydrin area = 1056.6064 (small front shoulder)
" 19.600" diol - area = 316.035
" 15.541" small peak over C 25 throughout Trans

9) Cool to room temp

10) Prepare a solution of 80g 50% NaOH (Baker lot # B4130) in 200ml H_2O. Charge dropwise, have temp < 30°C. Before charge, reaction clear, colorless. Begin 10:50AM. temp = 27.0°C. Became hazy after ~45 ml gn. No real exotherm, ~~11) Stir at room temp. for ~ 2 hours~~ 1C 4/16/96

Pull a GC sample to ~½ NaOH in see if epoxide is gone. Pull ~2ml dilute in methanol, shake. 1C 4/16/96 7-8ml sample. Filter through HPLC filter syringe. Sample clear & the most salts are out.

Date April 16, 1996 Signature Kevin T. Sudlets
Date April 16, 1996 Witness Rickelly

Cont page 24

10004-21 cont from p 21

8) Start to 8-22°C again w/ and condensation on temp 8:20AM. Pull a temp ~2hrs were 10:15 cut heat.

a) cool to room temp w/ nitrogen blanket stop mixed until I get results from 10004-2C.
Pull a GC sample & run on 10004-20 GC to see if I can verify the Rxn by GC

Seal Rxn w/ nitrogen blanket on it until I get results from 10004-2C

Cont page 28

Date April 16, 1996 Signature Kay Y. Swoller
Date April 16, 1996 Witness Rick Rich

10004-20 cont from 22.

Looks good. - peak at 5.20' carbohyd area = 1[illegible]9.8
4/14/96 " " 11.47 epoxide area = 732.0
" 14.08 chlorohydrin area = 72.3
" 17.49 "diene epoxide" - area - 124.4
" 19.61 diene - area = 2[illegible]0.16

- pull a sample after all NaOH in jar complete 11:50AM. Prep a buffered filtration
Seem to clear w/ clay. E2 helps interfere
peak at 5.303' carbohyd - area = 147.86
peak at 11.816 - mono epoxide - area = 1461.382
peak at 13.35 - chlorohydrin area = 96.93
peak at 16.11 - ??? area = 193.62
peak at 17.765 - di-epoxide - area = 401.569
peak at 21.27 - ??? triene? area = 61.29

11) 2:10 - 2 hr heat complete.
pull for another sample for GC
~~peak at 5.303' carbohyd - area = 147.86~~
~~" " 11.816' - mono epoxide~~ ICS 4/16/96
peak at 5.22' carbohyd area = 137.85
" " 11.74 epoxide area = 1460.52
" " 13.22 chlorohydrin area = 86.6
" " 16.07 ??? area = 204.43
" " 17.73 di epoxide area = 421.58 peak at 21.20 area = 21.20
Prepare for E2.
12) Charge 150 ml H_2O. 3:05pm
13) Heat to 65°C. for ~5 hrs
14) Phase in funnel 3:[illegible]0pm. At first (1st 5 min) Phase organic to med. brown organic layer a top, bottom (aqueous) layer has many colorless & small "blebs" falling to bottom. After settling the phases flip, organic layer falls to bottom.

Date April 16, 1996 Signature [illegible]
Date April 16, 1996 Witness [illegible]

Cont pg - 25

10004-20

Sand Rx n's leave in funnel overnight
There are some white salts in
organic layer, (NaCl?).

Date April 16, 199
Date April 23, 1996
Cont

Signature Kayle E. Sisodett
Witness Anna Chavez

10004-20 cont from pg 25

15) Drain ~~org~~ 1CS 4/17/96 organic (bottom) layer into a beaker - ~~58.6g~~ of tan, salty water removed c̄ some salts.

16) Transfer organic layer to a 500ml sep funnel.

17) Add 200 ml CHCl3.

18) Add ~~pt~~ ~210 ml HCl 1CS 4/17/96

19) Place ~45 grams 299.6g of bottom (organic) layer removed

Discard HCl (salts

20) repeat HCl wash X2 c̄ ~200ml H2O

21) Drain final organic layer into a 500ml Erlenmeyer RBF. wt of flask = 165.8g 1CS 4/17/96

wt of untreated material ~~= 165.8g~~ = 284.4g
~~pt~~ 1CS 4/17/96 flask + stuff removed = 222.2g →
56.4g

22) Start a GC as before in methanol

peak at 4.92"	area = 33.58	contaminant
peak at 11.27"	area = 511.13	monochlorohydrin
peak at 13.22"	area = 13031	mono - chlorohydrin
peak at 15.83"	area = 57.15	??
peak at 17.72"	area = 606.07	di epoxide
peak at 21.21"	area = 111.35	??
peak at 22.20	area = 9637	??

Date April 17, 1996 Signature Karen E Swallow

Date April 22, 1996 Witness Kirk Chavis

Cont pg 27

10004-26 cont for 2c

EZ extracts organic layer w $CHCl_3$. 1X3.

peak at 4.938 (calculated) –
peak at 11.59 (monoepoxide)
peak at 13.20 (monoepoxide)
peak at 15.958 ??
peak at 17.47 di epoxide
peak at 21.08 – ?? tri epoxide ?

No oxygen printed out. cont. quantitude but ratio of mono epoxide to di epoxide is about 8:1.

<u>131g</u> of clear, colorless material.

23) Pool both samples.
24) Check EEW on the pooled sample.
expect ~250. use ASTM method D1652-90
use 10ml buret #404, fill down & drain out when done, do not start point in this buret.
Sw1 = 0.4957g 0.1016N perch. Used 19.46ml of

$$E = \frac{4.3 \times 19.46 \times 0.1016}{.4957} = 17.15$$

$$\text{Meq} = \frac{43 \times 100}{17.15} = \underline{250.73}$$

expect – use buret #707 (50ml) for this one.
Sw2 = <u>0.4282g</u> Used <u>16.4ml</u> of 0.106 N perch

$$E = \frac{4.3 \times 16.2 \times 0.106}{.4282} = 16.58$$

$$\text{EEW} = \frac{43 \times 100}{16.53} = \underline{260.13}$$

Average – <u>255.4</u> not very good duplication.

Date April 17, 1996 Signature Kaye E. Siddett
Date April 22, 1996 Witness Lynn Chawla

10004-21 cont from pg 23

10) Prepare a solution of 96g H_2O & 43.2g 50% caustic. Charge slowly to Rxn & complete, ~~stirring~~ ICS & condenser & rx. Hold temp < 30°C before adding. Rxn is golden yellow/clear. complete 2:15 pm. Jovely.

11) Hold at room temp ~2 hours.

12) Have to leave, EZ to cut heat & put in fumes

cont pg 29

Date April 17, 1996 Signature Kenneth E Swedler

Date April 22, 1996 Witness Kathy Chavis

10004-21 cont from p 28

12) 8AM
Mixture in funnel, good phase
Top (organic) pale yellow, barely
better (H2O) in pale yellow, key c
Swirl at bottom

Phase & keep both ~~aqueous~~ layers for further work.

13) Add 400ml CHCl3 to organic layer
& 300ml H2O. phase in funnel 8:05A

14) Phase the aqueous layer from step #12,
& large 300ml CHCl3 phase in funnel 8:15A
Leave until tomorrow

cont pg 30

Date April 18, 1996
Date April 23, 1996

Signature Kay E Sirdar
Witness Lynn Chavis

~~Appr~~ KS 4/19/96 10004-31 cont from pg 29

15) want both Rxyn time X 20 cm before I am feeding the last extraction in the funnel, fill E2

Date April 19, 1996 Cont pg 31 Signature Kevin E Stillhart

Date April 23, 1996 Witness Lin Chaw

10004-21 cont from pg 30.

15) Phase & collect bottom phases of each.

~~Collect $CHCl_3$ layer from organic layer. 500ml 1 wash RBF. wt of flask = 145.7g~~

E2 already collected the layer

16) Collect the $CHCl_3$ for the organic material. wt of flask = 166.0g
steps

17) check epoxy equivalent wt of step 15 material. This material is pale yellow/clear
expect ee wt ~ 800.
ASTM method D 1652-96

$sw_1 = \frac{0.8725g}{\text{perchloric acid}}$ Dual 10.8ml of 0.1016N

$E = \frac{4.3 \times 16.8 \times .1016}{0.8725} = 5.4078$

$Weew = \frac{43 \times 100}{5.4078} = 795.15$

$sw_2 = \frac{0.8679g}{\text{perchloric acid}}$ Dual 10.7ml of 0.1016N perch

$E = \frac{4.3 \times 10.7 \times .1016}{0.8679} = 5.3861$

~~0.1N~~ 1054/22/55

$E_{Eew} = \frac{43 \times 100}{5.3861} = 798.35$

Avg ~ 796.75

0.01 C N perch = Aldrich lot # 14604KN
buret (some) #707

Date April 22 1996 Signature Kayce E Sudbeck
Date April 23, 1996 Witness Lynn Chavis

Cont page 32

10004-21 cont. from pg 31

18) weight of stripped material + flask from step #16 = 247.4g = 81.4g product.

19) check DV13 (P_2O_5) on product
Sw1 = 0.0436g = 0.0849% H_2O
off white clearly liquid.

20) check Epoxy equivalent wt. on the material

Sw1 = 0.8529g & used 11.9ml of 0.1016N perch.

$$E = \frac{4.3 \times 11.9 \times .1016}{.8529} = 6.096$$

$$E_{EEW} = \frac{43 \times 100}{6.096} = 705.4$$

Sw2 = 0.8307g & used 12.1ml of 0.1016N perch.

$$E = \frac{4.3 \times 12.1 \times .1016}{.8307} = 6.364$$

$$E_{EEW} = \frac{43 \times 100}{6.364} = 675.7 = 690 = EEW\ Avg$$

RAV say this is probably a mixture of monomer & oligomer. For E2 this is probably monomer. The material before E started EEW of 800 is mixture of monomer & dimer. But the monomer should be clear so filter ink a few

Date April 22, 1996
Date April 23, 1996

Signature Kayce Sutton
Witness Kim Chavid

Objective - Try to react an phenol with an epoxide, using KOH catalyst.

Procedure -

1) Equip a 250mL 3 neck r bottom flask with stirrer, N_2 heating & cooling. wt of flask & stir assembly = 266.3g

2) Charge 13.3g of phenol 10072-30 (mw = 149 = 0.0892 moles) with stirring. It is a dark brown thick liquid, with acid smell

3) Charge 100g (FW = 796.8) of epoxide 10004-21 (ICCS) = 0.125 moles.

4) 1054/14/98 Begin agitation & apply N_2 sweep. Epoxide & phenol readily miscible

5) Charge 0.29g of KOH pellet. Activ charge 0.5218g Dewes lot ?? wt a bottle, pellet, 3/4/96, w lot #.

Stop 5 min. Pull sample for HC. 0.3°C exotherm seen

6) Heat to 100-105°C r condenser. on temp 10:40AM.

7) While heating, run HC. Sample wgt = 0.5-.555 in 5 mL reagent, meth. per SPI100, glass, NOC on Perkin Elmer. HC. Start at 60°C, hold 2 min, 10°C/min to 300°C. Hold 5 min. Start 5 mL injection

Date April 22, 1996 Signature Kamyar Sweller

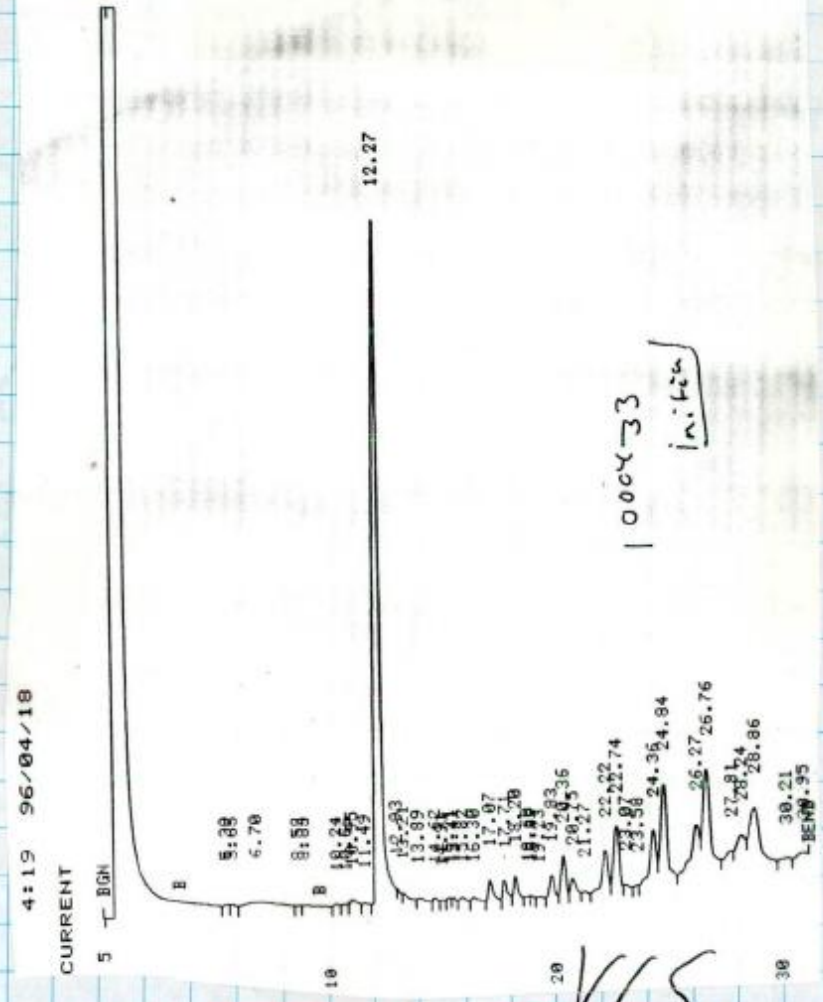
Witness Kim Chawla

Date April 23, 1996

Cont page 34

10004-33 cont. from p33

GC initial show large peak at 12.27 min
area = 569.79. Small double peak beginning at 17 min to ~28 min.



KCS

4:15 pull GC sample.
Seem [illegible] area = 581.79. still peak at 12.37

Leave on temp overnight, ☐ N2

Date April 22, 1996
Date April 23, 1996

Signature Kaye E Sudlett
Witness [illegible]

Cont page 37

Objective - React an Imide with polymeric epoxide using BF_3 catalyst.

1

Procedure -

1) Equip a 250ml 3neck with thermometer, stirrer, N_2 & condenser.

flask + stirrer = 302.3g

2) Charge 17.04g of Imide 9917-31 (RP) mw = 191 = 0.0892 mole. This is an off white, fine powder.

3) Charge 100g of polymeric epoxide (10004-21 ICS) ICS 4/12/96. EEW = 796.8 = 0.125 mole. Stir at room temp. & N_2 blanket ~ 5 minutes. Imide ~ 60% - 65% dissolves. Heat to ~ 50°C for ~10 minutes does not dissolve, Imide seems to aggregate into large clumps. Same at 75°C & 90°C. Stick to EC. There are large aggregates in Imide sample, & this is what seems to be aggregates now. Pk EC, mixture ~ 90 - 95% in solution

4) Cool to 25-35°C & H2O bath. Drop ~~5) Charge 0.5g BF_3 (1 Molar) ICS 4/12/96~~ out, Heat bath to 55°C. Too many

cont page 3C

Date April 22, 1995 Signature [illegible]

Date April 23, 1996 Witness [illegible]

10004-35 cont from p35

- Take to 75°C, slt milky

5) Try to add 0.5g BF3 (1 ml 0.0523 g) & lower temp ≤ 100°C. Probably very exothermic, will be difficult.
density of BF3 = 1.154 ∴ 0.5g = 4.5 ml.
Try to drop from 1 ml syringe
- begin at ~12:30pm temp = 74.2°C, add 3 drops, temp stays rising, drop rate levels at 80.3°C.
- Let temp drop to 78°C, add 3 drops, temp goes to 82.6°C.
- Put HC bath under RXN & temp drops to ~67°C, no precipitate, mixed water ne thick. Reaction is complete
- Remove HC bath & add in 3 drops in succession, only slt exotherm

Complete 12:40 pm. Tan, slt viscous, not any precipitate. Temp = 66.4°C. Cool down at 64°C & see a couple of small white opaque. Syringe add worked well

6) Heat to 70-80°C & hold ~4 hours, on temp 12:50pm. quick yellow.

at 1:45 when I return for lunch the RXN is dark red brown!!
at 2:05 pm pull GC sample
See page 33, step 7 for sample prep & GC set-up. Peak at 17.34 min for EL this is a wide. Sample started cooling before I could print report.

Stop last at 5:15pm. Seal the sample
Cont page 38

Date April 22, 1996 Signature Kurt Y Suzuki
Date April 23, 1996 Witness Kirin Chawla

10004-33 cont. from p 34.

Pull sample 8:20 pm. Mixing is orange/red, clear. Small change. Peak at 12.37" = 337.56 cm ~45% decrease since yesterday afternoon

3:20 pm pull GC sample
peak at 12.53" area = 308.1b.
No real change in peak at 20-28".
There is a change or clear separation, the front peak of the doublet is becoming the larger peak of the 2. Previously the second peak of the doublet was larger.
Also a peak is developing at 10.8"
area = 35.709

Stop feed 4:50 pm & seal in bucket

Continued page 40

Date April 23, 1996 Signature Faye C Sudlett
Date April 23, 1996 Witness Kim Chavis

10004-35 Cont. from pg 36

7) Heat up again 8 AM.

Prepare a mix in same ratio as initial sample & catalyst dissolve in methanol & run GC.

mix 1.74g Dmide & 1.6g epoxide to make
~~try~~ 0.174g Dmide & 1.0g epoxide in 11.7 ml methanol

large peak at 17.864 area -- 479.37 & small peak
Dmonitor ~20-28 min.
Dmonitor given that the Dmide peak from Yesterday sample is ~12 sec or the sample

10:15 AM pull a reaction sample for GC.
per usual before. Rxn mix is dark green/brown, the color of bile & slt viscous
peak at 17.857" area = 347.79.
& small peak at 20-28 min.
= ~25-30% decrease in peak for original. ~ Approx 20% decrease from 1st injection done yesterday

& do see a change in the small peaks for 20-28 minutes. They are now single peaks, they were initially doublets

Proceed to next step per EZ.

Cont. page 39

Date April 23, 1996 Signature Kayla C Swallett
Date April 23, 1996 Witness [illegible]

10004-35 cont. from pg 38.

8) Cool to ≤ 50°C.

9) ~~charge~~ 1054/23/96 Remove 0.5-0.7g for sample.

10) charge 100ml ethanol

11) charge 5.4g hydrazine hydrate. (Aldrich 09413LG) density = 1.029 ∴ charge 5.25ml.
Rxn mix becomes redder, lighter in shade & clearer.
~ 2°C exotherm. Stir ~5 min.

12) Heat to reflux. temp = 80.6°C time = 2:40pm
Reflux for 3 hours, Bpt ethanol = 78°C.
At initial reflux material is very thick with off-white solids. charge another 100ml ethanol so can stir.

After ~ 10 minutes at reflux the material dissolves & is brown & bubbly.

stop heat at 4:50pm & seal & seal under blanket

Cont pg 41

Date April 23, 1996 Signature Kenneth E. Miller
Date April 23, 1996 Witness Kim Chavis

10004-33 cont. from pg 37.

8) Per E2, go to deprotection step.
Transfer the RXN mixture to a ~~2 neck~~ KS4/24/40 1 neck 2 litre. put of 2 litre = 498.8g.
RXN mixture in a red orange hazy liquid
106.5g of RXN mixture transferred

I will need to eventually add ~2.5 litre of H2O & strip off to deprotect. Can do this in increments as I strip. Save H2O off. I can add some back if needed to H2O for disappearance of I white peak

for now add 750ml H2O

10:10 AM okay another 500ml

10:35 AM - charge another 750ml H2O.
* Empty receiver. The material is received has distinct benzaldehyde smell & is ~~slightly cloudy~~.

11:40 AM - charge another 500ml H2O & strip

9) Shut off - show no peak at 12 minutes previously no ~~double~~ KS4/24/40 chiralpak left.

(a) from DV TF 311 (chiralpak equivalent) & DV TF 12 (achiral/achiral) - DV TF 12 (achiral/achiral) - Sw = 3.4742g, & even 0.28 ml of 0.5N KOH (buret SF9601), achiral = 3.26

Cont page 45

Date April 24, 1996 Signature Kayne Swoboda
Date April 25, 1996 Witness Hecklitz

10004-35 cont. from pg 39

13) Heat back to refluxing. ~ total 9 hrs. 10:00 AM cut heat & cool to 5-10°C in 1 hr

14) Charge 8.92 ml muriatic acid slowly Dewey lot # X3016, complete 10:30 AM

15) Stir at 5-15°C for ~30 minutes

16) Strip at ~room temp in vacuum to remove some of the extra ethanol & hole filtration gauge. Not very successful at getting ethanol off

17) Filter - wash solid in ~300 ml ethanol.
The solid filtrate is waste, the liquid is raw product.

The solid waste is off white powder. Liquid (product) - 1st fraction is red/brown. Wash with ethanol to get the red/brown component out. 2nd fraction is light brown. Large is light brown.

~~18) In filter flask, charge~~ KS 4/29/96

(19) In the filter flask when I have collected my product, charge 7.2g of 50% Cantrol, white crystals.
Dewey lot # B4130. Off white precipitate (small amount) formed when Cantrol added, then redissolved.

20) Stripper wt of empty stripping flask = 272.1 g
flask + stripper product =

Date April 29, 1996 Signature Kayne Swedell
Date April 29, 1996 Witness Rick Ritz

Cont page 42

10004-35 cont from pg 4

21) Filter. Before filtration the Rxn is red, (brown solution, solution solution) observe a some of insoluble solid left off white filter

* Sample got from aspirator, some contaminants in some HCl & the dark

re-strip,

22) Check solution 0 (DV-13)
SW = 0.1437g = 0.2789d

23) Do anisine equivalent (DVII 311)
do not know what the equivalent should be, so weigh up ~ 1.0g first

SW1 = 1.0003g
glacial acetic, 15ml, lot #02621HN Aldrich

Dispense 1.8ml of 0.1016N perchloric acid
Aldrich #14604KN, lot #707 (50ml)

∴ anisine equivalent = $\frac{1.0003 \times 1000}{1.8 \times 0.1016}$ = 5484.5

now weight out using a sample wt of
4.0-5.5, SW2 = 4.4530g = 2624.4 ?
why the difference?

run a 3rd 1.5g sample wt ↑ sample weights
& increase acetic acid to get down error
SW3 = 2.3277g = 8.7ml = 2633.4 good.
Try one more ~ 0.5g sample wt. to get lighter color.

Date April 24 1996 Signature Kenneth Swidler
Date April 25, 1996 Witness Richards

Cont pg 43

10004-35 cont from p 40

sw = 0.4311g, we lower buret #404
I used 1.68 ml of perch.

amine equivalent = $\frac{.4311 \times 1000}{1.68 \times .1016}$ = 2525.7

I must have mis-read my buret on the first time. I am going to average, the 2nd & 3rd titration = 2628.9

Give info to E.Z. it is much too high. !! He says this

Run an acid a base # (DV TI 12)
~~sw = 3.6820g~~ ICS 4/24/96

~~sw = 5.7190g I used ~47.2 ml of 0.5N KOH (buret # SI9601)~~
~~Acid # = $\frac{47.2 \times .5 \times 56.1}{5.7190}$ = 231.5~~ wrong

do again - sw = 3.1579g we 1.23 ml of 0.5N color change in to orange from brown not pink
one strange titration ICS

$\frac{1.23 \times 0.5 \times 56.1}{3.1579}$ = 10.93

To correct amine equivalent do the following: don't know, Swift be with to talk about it.

- Now do acid base # (DV TI 12) on Jeffamine M-715 sw = 3.8662 turn pink, not I've a base #, we 3.56 ml of 0.1N HCl
I have # of 5.61.

Date April 24, 1996 Signature Kaye E. Sudlett
Date April 25, 1996 Witness Rick Lig

cont page 44

1004-35 cont from pg 43.

F2 did a "correction" of the amine equivalent found in acid/base info & got a corrected equivalent of 1481. He said that dirty & random & wide probably account for this.
Expected amine equivalent in 900-1000.
* Considering the sample removed for testing the stripped yield was 71.8g. & we have 48.8g in flask.
Transfer to labeled 1C2 for Correlation - worked relatively well here save dirty & save unreacted & wide causes a high amine equivalent & acid/base correlation

Date April 24, 1996
Date April 25, 1996

Signature Kaye E. Strobel
Witness [illegible]

10004-33 cont from pg 40.

Dr TI 311 - sw1 = 1.2992 g (See page 42 for ~~carbon~~ ICS 4/14/95 raw material lot #'s & buret #(s)
Titrated 9.2 ml of 0.1016 N perc
= 1389.93 amoxicillin equivalent

sw2 = 1.2773 g Titrated 9.1 ml of 0.1016 N perc
= 1381.52
Avg = 1385.73 amoxicillin equivalent

Give info to ER.
Stripped yield including samples removed for testing = 104.5 g.
Should have 98.4 g in flask. Transfer to labeled jar

See page 46 for Cy cam from this sample

Date April 24, 1996 Signature Kaye E Swedlet
Date April 29, 1996 Witness

Objective - Make a Cyan using formula 1004-33. Use sodium carbonate buffer & use 1 eq of CPC-SC to 4 eq. of amine. Corrected amine equivalent = 1150.

Procedure -

1) Equip a 500 ml 4 neck c̄ thermometer, stirrer, condenser, heating & cooling.

flask + stirrer = 437.1 g

2) Charge 42 g of amine (1004-33) amine equivalent = 1150 = 0.0365 moles.

3) Charge 4.34 g of sodium carbonate (mw = 106, = 0.0409 moles)
Denver lot V2582

4) Cool to 10-15°C c̄ agitation

5) Charge 0.25 X moles amount of amine, as CPC-SC
charge .25 X .0365 = 0.0091 moles. mw = 977 g/mole
8.89 g at 100% , use vendor lot # 9H3431.
This lot is 35.4%, = 25.1 g at 35.4% solids.
Charge, contents 9:35 AM temp = 8°C
w "chunks" of CPC SC.
pH = 8.27

Hold at ~10-15°C for ~30 minutes
10:05 AM pH 8.68
~~10:~~ 105 @ 25/4%

6) 10:10 heat to 80-85°C c̄ condenser
10:40 A temp = 79°C pH = 7.67.
Keep on hold ~3 hours.

Date April 28, 1995 Signature Kenneth E. Stoller
Date April 29, 1995 Witness [illegible]

Cont page 47

1004-46 cont from p 46

7) 1654/4/25/96
11:25 AM pH = 7.99
1:10 pm pH = 8.30 ? going up temp = 81.3°C

7) 1:40 pm cut heat, & charge 65g of H2O. stir 5 min & check pH.
after 5 min = 9.13,

~~8) Adjust pH to 10-11 c ogen ammonia~~ 1645 4/25/96

8) check CV & wt. of material
flask product = 569.5g = 132.4g material

check DV383 (CV) in material –
sm1 = 0.4863g flask # 712 flask # 673, 2nd transfer
λmax = 665.5 abs = 1.0115 CV = 10.4
shoulder at 599.5 abs = .2170

sm2 = 0.5396g flask # 951, 2nd transfer # 685
λmax = 665.5 abs = 1.1319 CV = 10.5
shoulder at ~~9957~~ 1654/4/25/96 599.5 abs = .2422
looks good Avg CV = 10.5

10.5 X 132.4 = 1390.2 & mat 1654/4/25/96 8.7g
CPC-SC at 100% ÷ Phase 147.1 156.4 conversion unit/gen

9) Adjust pH to 10-11 c ogen ammonia
Reactor wt 2378g, after 1.3g ammonia
pH = 10.18

10) Adjust pH to 6.5-7.5 c 85% H_3PO_4
Reactor wt 4007g pH = 6.65 after 3.2g
85% H_3PO_4

11) Heat to 70-75°C for ~ 15 minutes
12) Phase, & funnel 3:00 pm

Date April 25, 1996 Signature [illegible]
Date April 29, 1996 Witness [illegible]

Cont page 48

10004-48 cont from p 47

at 4:44 see same pharmacy, let set overnight per EK

Date April 25, 1996

Date April 29, 1996

Signature Kaye E. Sisskette

Witness 28 M

Cont page 49

10004-46 cont from pg 48

13) ~~Collect phase: bottom (product) =~~ ICS 4/26/96

13) Per FR charge in phase, collect entire mix, charge 10g sodium sulfate ICS 4/26/96
Rinse beaker w 10g H_2O. charge 7.0g of sodium sulfate (Dewey lot U2503)

14) Heat to 70-75°C & phase on funnel 9:25 A.

10:30 AM Transfer to phase
Bottom (H_2O) = 57.6g & dark blue, thin interface
57.1g product (top)

15) Transfer product to 3 neck & extract twice using 70ml H_2O & 7g sodium sulfate. Do not do pH adjust, check pH once w temp & sulfate to solution. pH = 10.0

While heating up, check DV383 on water layer from step #14. Run in nutsonol

SW1 = ~~0.84~~ ICS 4/26/96 0.6208g flask #712, 2nd transfer (white precip.) to flask ~~726~~, λmax = 665.5, abs = .6498
CV = 5.23 shoulder look normal.
SW2 = 0.7272g flask #309, white precipitate 2nd transfer to flask #673, λmax = 665.5 abs = .8124
CV = 5.59 Avg CV = 5.41

16) P have 2nd washed in funnel 11:30 AM
500ml 1m sepanta. Drain top (product) into c
Bottom (H_2O) = 23.2g dark blue, thin.
145.3g, 104g unstripped product

Date April 26, 1996 Signature [illegible]
Date April 29, 1996 Witness [illegible]

cont page 51

objective - Run a Cyan using SEO Amine & PEG 400. Use 4EQ amine / 1EQ CPC-SC.

Procedure -

1) Equip 500 ml 3 neck r.b. thermometer, stirrer, condenser, heating, & cooling. flask + stirrer = 338.7g

2) charge 25.7g of SEO amine 9988-55 (This is a red/brown slt viscous liquid in a nearly sealed) use amine equivalent of 257 = 0.1 mole.

3) charge 11.94g sodium carbonate (0.1126 mole). Reg V2582
4) Charge 26.5g of PEG 400 = 0.065 mole. Amin Exhibit 5427C13
5) Cool to 10-15°C w/ agitation.

6) Charge CPC-SC; 0.25 X molar amount of amine, .25 X .1 mole = 0.025 molar (mw = 972) = 24.4g at 100% the vendor lot # 9H343 (Aric Rel Freeze) This material is 35.4% soln. ∴ Dissolved (0.1c 4/26/96) 68.9g at 35.4% Actual charge 69.6g. Complete 9:10AM temp = 7.4°C, no problem blue a few lumps

Stir ~5 min - pH = 9.57
9:40pm - temp = 15/10°C pH = 8.86

7) 9:45A heat to 80-85°C w/ condenser, problem w/ heating mantle, not a temp control
10:45AM pH = 7.72.
hold ~ 3 hours 11:30 pH = 8.25, temp = 82.3°C
pH at 1pm - 9.19 1c 4/26/96 8.63.

Cont page 52

Date April 26, 1996 Signature [illegible]
Date April 29, 1996 Witness [illegible]

1004-46 cont from pg 49

17) Strip product ~ 5 hrs

Check CV on Hrg layer from strip 16.
for DV383 in nutsent
sw1 = 0.8600 flnl #673, 5 ml transfer to flnl # 695.
λ max = 665.5 abs = 0.6591 CV = 1.53
shoulder looks slightly elevated

sw2 = 0.8024g flnl # 309, 5 ml transfer to flnl #951, λ max = 665.5 abs = .5681 CV = 1.42
Avg CV of Hrc layer = 1.48.

wt of flnl + stripped product = 193.0g = 47.7g
stripped product.

check Eotrc (DV13) – sw1 = 0.0847g = 3.3299%

sw2 = 0.0255g = 3.567%

re-strip Monday

Cont page 53

Date April 26, 1996 Signature Kay E Sudbeck
Date April 29, 1996 Witness JBrue

10004-50 cont from pg 50

11:55pm - pH = 8.66 temp = 81.0°C

8) 2pm Cut heat & allow to cool to ≤ 50°C

Get wt of Rxn mixture + flask = 462.5g
i.e. charge 123.8g product (but pure, some spill at edges)
* Product has very distinct fenugreek smell.

stir ~8 minutes after weighing & get a CV (CDV383) in methanol.
Sw1 = 0.5658g flask #2421, 2nd transfer to flask #695
λ max = 665.0 abs = 2.8458 CV = 25.15
sw2 = 0.3911g flask # 789, 2nd transfer to flask #309
λ max = 665.0 abs = 2.0695 CV = 26.46
Avg CV = 25.81
So both dilutions the standard curve is too ↑ in absorbance.
Yield = 123.8 X 25.81 = 3195.28. D used 24.4g CPC-5c
wt 100% = 130.95.

9) 2:40pm charge 90g H_2O & 15g sodium sulfate (Baker lot # V2503) -

10) Heat to 80°C for ~5 minutes

11) Transfer to sep funnel at 3:20pm

Secure until Monday

Cont page 54

Date April 26, 1996 Signature Kurt Swedberg
Date April 29, 1996 Witness

10004-46 cont from pg 51

18) Chg 5 ml ~~filtrere~~ & re-strip

19) Check DV13 (H2O by Aquatest)
SW= 0.065g -1.4490 I have stopped
for ~~1 sloun~~ at 90°C. Can't get any lower

20) Final strippe sample = 191.7g = 46.4g product.

21) Check DV B83, in methanol.
~~Sw= 0.2267~~ 1CS 4/21/86
SW1= 0.1372g flask #C93, 2 ml transfer to #726,
λmax = 666.0 abs= .5357 CV= 19.52

SW2= 0.3460g flask #309, 2 ml transfer to #88C,
λmax = 665.5 abs= 1.3305 CV= 19.23
Avg CV= 19.38, not corrected for Et2O

material dissolves well in methanol.

The slowly over below 600-650 looks a little high. Save to look on 00446 Submit for Nat.
Transfer to 40 for Jim & Sunwing for F2.
Yield = 46.4 x 19.52 = 899.232, This gives 101.2 conversion with 100% g of CPC-5C.
Caution - The yield is slightly lower than standard! I do not know ~~expected~~ if the shade is acceptable until after extraction 1CS 4/21/86

Note done yet, see pg 61 for more work

Date April 29, 1986 Signature Carl E. Schiller
Date April 29, 1986 Witness [illegible]

1004-50 cont from p 52

There are 3 layers in sep funnel.
- bottom is ~ 7ml of dark organic material.
This layer is soluble in same salt aqueous

- Collect middle, primary organic layer in ~~a beaker~~ LCS 4/29/96
a 500ml round bot or 1 ~~neck~~ = LCS 4/29/96 rotovap flask =
156.5g 99.6g dark blue salt viscous
material collected, * strong benzaldehyde odor

strip organic layer

~~- Top (2nd organic layer) = 111.1g dark blue,
thin material, moderate benzaldehyde odor.
check CV (DVS 63) in methanol,
SW1 = *0.6718g flask # 726, 2ml transfer to
# 695 ~~λ max = 0.9842~~ abs = LCS 4/29/96
~~λ max = 668.0~~ ~~abs = .8246~~ wrong value in UV

SW2 = ~~0.8182g~~ LCS 4/29/96 *0.8186g flask # 242
2ml transfer to # 951.
KS/ 4/29/96~~

* white precipitate seen in initial dilution

re- dilute CV's, Sonicate, put
aqueous in the methanol bottle!!
Get methanol myself & re-dilute
SW1 = 0.7404g flask # 309, 2ml transfer to flask
#695 λ max = 666.0 abs = .3150 CV = 2.13
verbal scan,
SW2 = .6407g, 2ml transfer λ max = 666.0, abs = .3450
abs = 2.69, (Aus CV = 2.41)

Date April 29, 1996 Signature Kevin E Szalkowski
Date April 29, 1996 Witness [illegible]

Continued page 57

Objective – Run a cyan energy amine 10067-36 (EX2). The an amine equivalent of 466, we YEQ of amine per 1 equivalent of CPC-SC. The YEQ Na_2CO_3 / 1 equiv CPC-SC to buffer. (This is a hydrogenated benzylamine
ICS 4/30/96)

Procedure –

1) Equip a 250 ml 3 neck r bottom flask, stirrer, condenser, heating & cooling, wt of flask + stirrer = 290.4g

2) Charge 50g of amine 10067-36 (EX2), this is an amber / slightly hazy liquid, has some very fine black particulate in it. Has a faint odor that I think may be toluene. ICS 4/29/96 The amine equivalent wt of 466, ∴ 50g = 0.1073 moles

3) Charge the same moles equivalent of sodium carbonate. .1073 moles at mw = 106 = = 11.375 (Barney lot A3948) Actual charge = 11.65

4) Cool to 10-15°C agitation.

5) Charge 0.25 X molar amount of CPC-SC, mw = 977. = 0.0268 moles, at 100% solids. The vendor lot # QH3431 (Hi Tol Pharma) which is 35.4% solids. ∴ I need 26.2g at 100% solids or 74.0g at 35.4% solids.

Begin charge 11AM temp = 13.2°C, complete 11:10AM temp = 10.7. Stir 5 min & check pH. pH = 9.35 temp = 13.0°C. Hold ~30 minutes at 10-15°C.

Date April 29, 1996 Signature Kaye C Sudlet

Date April 29, 1996 Witness [illegible]

Cont

pg 55

1004-55

6) 12 noon heat to 80-85°C
~ temp 12:30 p temp = 80.6°C,
pH = 8.49

3:25 pm temp = 80.6°C, pH = 8.68
Dark blue, early stirrable liquid

7) 3:30 cut heat & cool to <50°C,
weigh flask. Flask + product = 395.6g
= 105.2g of product.

Stir ~5 min.
Check DV383 in methanol, sw1 = 0.4147g
flask #695, 2nd transfer to #726
λmax = 665.5, abs = 1.5372 CV = 18.53

sw2 = 0.4130g flask #2421
λmax = 665.5 abs = 1.5172 CV = 18.33
Avg CV = 18.33
Shoulder over between 600-650 nm in elevated
Yield = 18.33 X 105.2 = 1928.3 = 73.6 units/g CH-54
8) Charge 75g H2O to RXN & stir ~5 min
pH = 9.87.

9) Adjust pH to 10-11 c aqueous ammonia
Dainty pH # 23789, after 3.7g pH = 10.12

10) Adjust pH to 6.5-7.5 c 85% H3PO4,
Dark red A4007, Foam moderately & white precipitate (a small amount) formed,
after 10.9g pH = 7.56

Date April 29, 1995 Signature Kayne E. Swadlett
Date April 29, 1996 Witness [illegible]

Cont pg 58

10004-50 cont. from page 54.

12) Check DV13 (5% H_2O) a stripped sample

Material is very viscous, heat up sol can sample

sw1 = 0.0922g = 1.325% H_2O
flask + 5 stripped sample = 215.4g = 58.9g product

13) Check DV383 (CU) in methanol.
Had to sonicate into solution
sw1 = 0.3147g flask #673, 2 ml transfer to #712. λmax = 665.0, abs = 2.9263 CU = 46.5
Absorbance is ↑ than optimum

sw2 = 0.2384g #726, 2 ml transfer to #747.
λmax = 665 abs = 2.3243 CU = 48.7

* "shoulder" over a much ↑ than a both scan from normal

Repeat 2nd dilution a sample #1, transfer 1 ml
λmax = 665.5 abs = 1.6103 CU = 51.2

Avg = 51.2 + 48.7 = 50.

Still some benzaldehyde odor

14) Heat sample to ~100°C & pressure filter through a 0.2 micron filter (I am not sure this is 0.2, not well labeled) into an 8 oz jar. Jar lid = 151.8g. Need heat & ~30 psig to get it through filter. I have 38g filtered material. See back of A

Date April 29, 1996 Signature Kaye E Sickler
Date April 29, 1996 Witness

See Continued page 69

1004-55 cont from pg 56

11) Heat to 70-75°C. for 1 hr under

12) Pour into sep funnel 5:30pm
Seal under AN

Continued page 59

Date April 27/1996 Signature [illegible]

Date May 7, 1996 Witness [illegible]

1004-55 cont. from p 58

13) Drain phases good separation

Bottom (H2O) = 74.4g pale blue liquid

check DV 383 (CV) in nutrient –
SW1 = 1660g flask #717, 5 ml transfer to # 889,
Top layer used initial dilution
Mwater 665.5 abs = 0.4311 CV = ~~0.2597~~ 1.04 5/4/95 CV = 0.037
SW2 = 1.9757g flask #695 5 ml transfer #677
Top layer used initial dilution.
Mwater = 665.5 abs = .7094 CV = 0.036
Top (product) = 110.5g thick blue liquid.
VCG 4/30/95
white precipitate in dilution

14) Reflux work.
pH = 8.56.
– adjust pH to 10-11 2 aqueous ammonia (same lot) – after 11.4g
pH = 10.10
– adjust pH to 6.5-7.5 2 85% H3PO4 (same lot)
after 12.2g pH = 7.29
very little foaming
– heat to 70-75°C for ~ 5 minutes
– Transfer to sep funnel 9:35AM

15) Separate phases 11:40AM

Bottom (Product) = 61g of dark blue viscous liquid
Drain into a 1-neck RB flask wt of flask – 173.2g

Top (H2O) – other phase (weak color) having a lot of product here. Drain 139.2g check CV (DV383)
SW1 = 1.6980g flask #724, 2 ml transfer to # 726,
Mwater = 660.0 abs = .6245 CV = 1.84
SW2 = 1.9455g flask # 889, 2 ml transfer to # 677, Mwater = 666 abs = .7995 CV = 1.82

Date April 30 1995 Signature Kuper & Sutcliffe
Date May 7, 1995 Witness Kim Chawla

Cont. page 60

10004-55 cont from pg 59

(c) Strip product for ~4 hour at 85°C.

17) Cool flask & get weight.
flask + stripped sample = 208.6g.

material is dark brown very viscous but fairly flowable at room temp = 35.4g of stripped product.
* There are several small "chunks" of solid, brittle material, Try to remove these from sample.*

18) Check 90 H_2O (DV 13) on stripped sample
Sw1 — 0.0644g = ~~0.0704% H2O~~ 1/5 4/30/95 0.7049%

Sw2 = 0.0573g = 0.6939%
Avg % H_2O = 0.6999% H_2O

19) Check DV383 (CV) on sample, in methanol
Sw1 = 0.2367g flask #747, 2 ml transfer to flask # 309, l_{max} = 665.5 abs = 1.9802
CV = 1.9802/.2367 XS = 41.8

Sw2 = 0.2192g flask #889, 2 ml transfer to #673, l_{max} = 665.0 abs = 1.8521

CV = 1.8521/.2192 XS = 42.2
Sample over between 600-650 λ is elevated

* The solid material is white with color is masked off but only moderately H2O soluble

~~SP~~ 1/5 4/30/95

continued page 62

Date April 30, 1996 Signature Gary E. Sudlett
Date May 7, 1996 Witness Lynn Chavis

10004-46 cont from p. 53

22) E2 you want the bulk filtered. Filter through at 0.2 micron filter into an 402 jug. Put lid = 97.0g. Heat sample to ~100°C & use ~30 psis pressure. Filter well.

Jug + lid + filtered sample = 118.0g ~ 21g filtered

Check CV (DV 383) on filtered material in methanol
Sw1 = 0.12575 flask #886, 2 ml transfer #951
λ max = 665.5 abs = 0.4883 abs/sw CV = 19.42
CV = abs/sw × 10/aliquot volume = abs/sw × 5 :

Sw2 = 0.22965 flask # 309 2 ml transfer #695.
λ max = 665.5 abs = 0.8934 CV = 19.46
Avg = 19.44

Check DV13 (C6H6) on cooled sample
Sw1 = 0.0492g = 2.5375%

Sw2 = 0.0711g = 2.7589%

Picked up the on filtering,
Sodium before filtering = 40186.6 ppm (report #1567)

Submit a filtered sample for sodium
Sodium after filtering = 39189.1 ppm (report #1568)

Color value did not increase. Check filter to make sure it did not plug filter. Filter is intact.
Check DV BC (C6H6) once more after sample has cooled ~2 hours Sw = 0.0568 + 2.7012% H2O

Date April 30, 1996 Signature Gene E Swezler
Date May 7, 1996 Witness Kim Chavis

10004-55 Cont from pg 60

19) Pr Er methanol remove filter through filter paper

- Heat the material to get of flammable transfer some to an 800ml beaker equipped with a magnetic stir bar

Wash with ~500ml methanol & filter discard filter a 1 litre crack
wt of 1 litre = 260.5g

20) Strip methanol

Seal until tomorrow

Cont page 63

Date April 30, 1996 Signature Kayo E Suzuki
Date May 7, 1996 Witness Kim Chavis

10004-55 cont. from pg 62

21) check DV383 (CV) in neltland
sw1 = 0.1887g flask #747, 2nd transfer to
#889. λmax = 665.5 abs = 1.5772
CV = $\frac{1.5772}{0.1887} \times 5 = 42.17$

sw2 = 0.1627g flask #673, 2nd transfer to
flask #951. λmax = 665.0 abs = 1.3914

CV = $\frac{1.3914}{.1627} \times 5 = 42.76$
Avg = 42.5

should run between 600-650 because elevated

Some Scan #2 to check on 00455

22) check Soltice (DV13)
sw1 = 0.0915g = 0.2329%

23) Submit small sample for sodium

Submit sample for testing in PET.

~~Sodium result = 1/5/96 832.3 ppm~~ 1/5/96

See pg 68 for sodium results

Date May 1, 1996
Date May 7, 1996

Signature [illegible]
Witness [illegible]

10004-56 cont from p 57

15) check % thc ~~(DV383)~~ KS 9/30/96 DV13
sw = 0.0993g = 1.166%

16) check CV (DV383) in methanol
sw1 = 0.1025g flask #683, 2 ml transfer to #309.
λmax = 665.5 abs = 1.1111
CV = $\frac{1.1111}{.1025}$ X5 = 54.2

sw2 = 0.1105g flask #695, 2 ml transfer to #885
λmax = 665.5 abs = 1.1525 CV = 53.5
Avg = 53.9

shoulder over between 600-650 nm ↑.
Save to dry a ~~0450F~~ KS 9/30/96 0450F
Sodium = 13059.4 ppm (report #1568)

Conclusion:

Color value acceptable, potency not very good, strong benzaldehyde odor.

Date May 1, 1996 Signature Kay E Sickler
Date May 7, 1996 Witness Kim Chavis

objective - react perosethanolamine with phthalic anhydride, to produce 2-hydroxyethylphthalimide to hopefully make a Jeffamine replacement

Procedure

1) Equip a 3 liter RB 3 neck c thermometer, stirrer, and heating fleck & stir assembly = 700.0g

2) Charge 305g of perosethanolamine (m.w. = ~~148~~ 61 = 5 mole) to flask. Also called ethanolamine. Added lot # 01606MP (99%) ∴ I used 308g at 99%.

3) Heat to 85-80°C. Do not condense, we want H2O to come off.

4) Slowly charge 740g of phthalic anhydride (This is a solid powder) m.w. = 148 = 5 moles / CS 8/1/96
Added lot # 0944PG = 790.4g
Density lot # 51969 - 444.6g

Do not exceed 130°C, sprinkle in from spatula

Begin charge 11 AM temp = 77.9°C, not heating, big to hold c water. Very exothermic

Appx first 250-350g in solution became very golden in color & clear. Following

Date: March 1996 Signature: George E. Swedler
Date: May 7, 1996 Witness: John Chando

Cont page 65

10004-65 cont from 59

- After ~400g anhydride in, the solution is quite yellow, slt hazy viscous & some flake of anhydride in a clear solution, exothermic.

- After ~ another 75g (~475 g Total) the reaction becomes cloudy & do not see chunks of anhydride, the mix just became opaque & is much less exothermic. Warm.
- Charge removed quickly little exotherm

Charge complete 12:35pm - temp = 94.6°C

max reaction temp seen - 108.9°C
min " " after charge started = 92°C
No heat required during charge

5) Heat to 110°C for ~2 min to make sure anhydride is reacted. Then heat to final temp of 128-133°C.

* ER says the product in formula does not melt until ~125°C. Donut cutterne.

On temp 1:10 pm - clear, golden brown set viscous.
2:30pm became very darkly colored set cloudy

Start a GC sample. ~0.3g in 4 ml vegetable sample from a vial as soon as taken out. Sonicate to dissolve. Start 0.5 ml.
SP 2100 glass WCC column 60°C for 2 min, 10°C/min ramp to 300°C hold 10 min. Very large peak at RT 19.28'' very small peak at 21.22'', 26.79'' & 30.51''

Date May 1, 1996 Signature [illegible]
Date May 7, 1996 Witness [illegible]

Cont pg 67

10004-65 cont from p 65

6) EZ finished Rxn by ~~[illegible]~~ 1 ~~55~~/2/86 cooling to 70-80°C & charging 1 blue H_2O

7) Heat then refluxed for ~ 1 hour to re-crystallize, filtered & washed for to get off white small crystals.

8) EZ placed the crystals in a 110°C oven overnight.

9) This morning I will resume Rxn. Start GC & same parameters as before, except start only 2-3 ml injection. Too concentrated and ~ 5 ml acetone & re start

Only one peak besides solvent, at approx at 18.03'' area = 89.97

10) Weigh so solids (DVH) ½ g / ½ hr, 5 pans over # 00501 110°C.

pan #1, empty wt = 1.106 g sm1 = 0.5157 g, pan + dry = 1.6159 g = 98.86 %

pan #2 empty wt = 1.0985 g sm2 = 0.5144 g pan + dry = 1.6099 g = 99.42 %

pan #3 empty wt = 1.1014 g sm3 = 0.5105 g, pan + dry ~~1.6160~~ 1 ~~55~~/1/96 1.6057 g = 98.79 %

pan #4 empty wt = 1.1007 g sm4 = 0.4978 g, pan + dry = 1.5925 g = 98.79 %

pan #5 empty wt = 1.09[illegible] g sm5 = 0.5187 g, pan + dry = 1.6073 g = 99.48 %

AVG % solids = 99.19 %

Calculation = ~~dry wt 1 ~~55~~/1/96~~ $\frac{(\text{pan + dry sample wt}) - \text{pan wt}}{\text{sample wt}} \times 100 = \%\ \text{solids}$

Date May 2, 1996 Signature Kevin E Swidler

Date May 7, 1996 Witness [illegible] Chavis

10 004-55 cont from p 63

Sodium result - 832.3 ppm (report #15772)

Calculate conversion before methanol wash/filtration,

35.45 X 42.02 = 1486.8 g used 26.25 of 100% CPC-SC
= 56.75 units/gen CPC-SC

Summary - for conversion:
Summary sheet to F2

Date May 7, 1996

Date May 7, 1996

Signature [illegible]

Witness [illegible]

Objective – Try to make an alkylated amined replacement for Jeffamine M715 using an F mole, treated c̄ KOH

Procedure –

1) Equip a 500 ml 3 neck c̄ thermometer, agitator, condenser & heat.

2) Charge 100g of amine 10000-27 (EXL) MW = 440 = 0.227 mole. Begin agitation. This is a dark yellow/brown liquid. Slightly oily. Slight ammonia odor. Flask + stuff = 338.0g

3) Charge 100ml H_2O dissolve/mix well. Exotherm about 8°C.

4) Charge 70.8g of KOH (45%) Dump but ?? no ~~KOH~~ a bottle! Charge over ~10 minutes. Very exothermic

5) Heat to reflux. Begin refluxing slightly at ~92°C. Then keep going up. Reflux well at ~114.2°C. Continue 3:10pm. Broaden (not long) then liquid. Stop heat at 117–118°C. Monitor by GC.

Sample for GC 4pm
part ~~0.3–0.5g sam~~ KOH 5/2/96 4 drops sample in 5 ml volumet flask. Shake well.
SP 2100 fused silica column, Perkin Elmer 8500 GC.
60°C for 2 min ramp at 20°C/min to 200°C & hold 10 minutes. Take look, put about 1g in 5 ml & shake 5 ml. Permit re-sample.
Re-sample at 5pm & see if more conventional sample Cent
page 74

Date May 2, 1996 Signature Carl E Sroller

Date May 7, 1996 Witness Lisa Chawis

Objective - Try to make an alkoxylated amine to use as a surfactant from Exp. I mixture (10000-27 Exp 2) and butyl glycidyl ether & BF_3 catalyst.

Procedure

1) Equip a 250 ml 4 neck flask w/ thermometer, agitator, heat, condenser & N_2.
flask + stir assembly = 317.0 g

2) Charge 100 g of ~~amine~~ (#10000-27) 10/5/96 as made. Dark yellow/brown, set viscous, set toluene odor. Begin agitation & N_2 sweep. MW = 440 = 0.227 moles

3) Charge 2 g of BF_3. Aldrich lot # 05523AQ
density = 1.15 g/ml ∴ 2 g = 1.73 ml Charge by pipet.
~2°C exotherm

4) Heat to 50°C. Frothing ~10°C above set point. Heat up ~~factory~~ 10/5/96. & a BF_3 catalyzing a raw material sp. Rxn?

5) Add a total of large butyl glycidyl ether - 38.4 g (0.295 moles). Do not exceed 70°C. Lot # indicated on bottle.
Begin add 3:30 pm temp = 53.2°C
completed 4:25 pm temp = 66.2°C
max temp during add = 69.2°C. More exotherm than 1/2 of add. Rxn mix is slightly hazy hours later were viscous now.

6) Heat to 70-80°C for 4 hours. Heat cut by EZ.

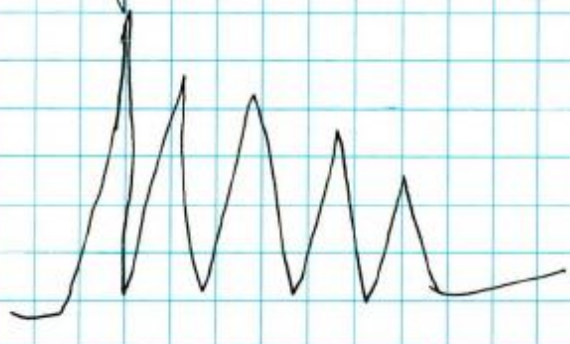
Date May 7, 1996 Signature Eugene E. Swartzlett
Date May 7, 1996 Witness Kim Chavis

Cont page 72

10004-69 cont from p 69

The [illegible] may have a sour [illegible] cents
So Run [illegible] in chlorofm ~1g sample is
about 5 ml.

Show multiple peaks
0.005" larger 8.00", 9.950", 11.563", 12.957"
peaks descend uniformly.



E2 says he does not understand the
ratio & the peaks he expected a binomial
distribution.

Stop test at 9:30 pm by E2

Cont page 75

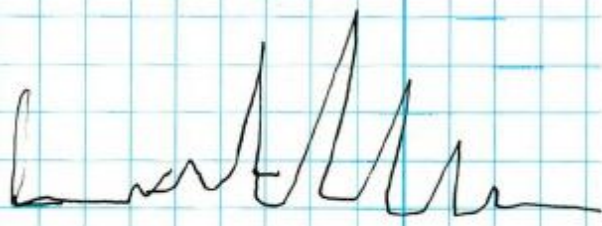
Date May 2, 1996 Signature Kaye E Sudbeck
Date May 7, 1996 Witness Kim Chavis

10004-70 cont. from pg 70

7) ~~Stu~~ BCS 5/3/96 Re-run GPC on curve using 50°C for 2 min / 10°C/min to 300°C, hold. Since when the samples are run (Rxn mixture) in CH_2Cl_2 we get very odd GPC traces. Run the sample in methanol & see how it looks

Inside in methanol show a good almost bi-modal distribution.

peaks at 11.66" area = 17.3009
13.70" area = 49.6780
17.81" area = 80.8160
19.82 area = 86.0425
22.45 area = 170.2120
24.88 area = 256.5831
26.99 area = 186.3891
29.36 area = 110.7703



Rxn mixture in methanol (concentrated sample) show many small peaks to shoulder below 4.4" & 24.7". They are not really in a bimodal distribution

peaks at RT 4.415" area = 39.43
9.573" area = 91.4995
11.886" area = 68.229
15.865" area = 89.885
17.881" area = 41.8946
19.258 area = 39.4644
20.513" area = 34.587
22.955" area = 28.7913
24.207" area = 30.7372

The sample is very concentrated, so that there may be more oligomers. The product m.w. is probably so ↑ that it will not show up.

Date May 3, 1996 Signature Gary E. Sudlett
Date May 7, 1996 Witness Ann Chavis

Cont pg 74

Objective - Try to make a
Jeffamine replacement from Jeffamine 10 000-27
by deprotection with hydrazine hydrate.

Procedure

1) Equip a 500ml 3 neck r bottom, stirrer, condenser & heat.

flask + stirrer = 427.2g

2) Charge 100g of Jeffamine 10000-27 (Jeffamine) mw ~440
= 0.2273 moles (brown/yellow liquid slt bitter odor)

3) Charge 200ml ethanol.

4) Charge 13.22g (55% active) hydrazine hydrate.
mw = 32 = 0.2273 moles
Aldrich lot # 09413LC. before hydrazine charge temp = 19.2°C exotherm quickly to 28.9°C
5) Heat to reflux. Gas temp 79.5°C
10:10 AM. Pink mixture to non tan/yellow liquid & milky like weak coffee c̄ cream
Took on stirring ~ 1 hour.

6)

c) 11:30 AM Shoot a GC sample in methanol.
SP 2100 glass WCC column. P-E 8500 GC
60°C for 2 min, 10°C/min to 300°C, hold at 300°C for 5 minutes. ~0.1g in 2ml of reagent methanol, 5 ul inject
- On second thought shoot a "neat" 3ul injection
Won't work have to dilute further in methanol

Date May 3, 1994 Signature Guy E Sadler
Date May 7, 1994 Witness Lisa Chavis
Cont. page 10087-1

10004-70 cont from pg 72

Per E2 bgt wt of material, transfer to flask & stirrer & product = 454.8g

Send ~25 sample for NMR

Rxn material to clear yellow c̄ slight ~~bright~~ glycidyl odor.

Wait on C13 & 1H NMR results

Date May 3, 1996

Date May 7, 1996

Signature Kaye E Swatlett

Witness Kim Chavis

10 00469 cont. from pg 71

9AM Start another GC on sample
60°C for 2 min, 10°C/min → 300°C.
Hold at 300°C for 5 min

- Reactions appear complete now find a GC
KSS/3/96 there is an almost bimodal distribution that looks almost identical to Smoke except shifted forward (the major ~~Starting~~ KSS/3/96 product will be ↓ than inside)

peak at RT - 7.873" area = 195.1182
RT - 11.440" area = 160.957
RT - 14.797 area = 233.63
RT - 17.874 area = 171.4932
RT 20.555 area = 76.2919

small shoulder on each peak, 1st 2, shoulder front last 3 shoulder tail.

7) Heat to 75-80°C for ~5 minutes. Try to phase. Keep both aqueous & organic phase for now until we can analyze

put in sep funnel 12:05 PM
Begin filtering almost immediately Very good phase

- 1:05 pm collect bottom (Aqueous) layer
put in sealed jar bottle 10004-69 aqueous layer #1, 168.7g of red yellow clear material.
Top (organic) layer is red/brown, set viscous, 85.8g
Drain top layer into 2 neck RB.
Save the H2O layer

8) Charge 100g H2O & 10g sodium sulfate to organic layer & heat to 75-80°C ō agitation
sodium sulfate in Dewey Rxt U 2503

9) Phase ~ 1 hour. Top (organic) = red brown set bubbly
Bottom (H2O) phase ō off white solid

Date May 3, 1996 Signature [illegible] & Swedlet
Date May 7, 1996 Witness Lynn Chavis
Cont ~~10 0087~~ KSS/3/96 10087-3