Supplemental Original Notebook Chemical Shift Data Supporting J.H. MacMillan and S.S. Washburne, "Lanthanide Chemical Shift Reagents as Tools for Determining Isomer Distributions in 2,4-Hexadieneoates and Related Compounds" Organic Magnetic Resonance, Vol. 6., p250, (1974).

This research was performed at Temple University in 1973, sponsored under Grant No. CA-13120-02 from the National Cancer Institute.

The original notebook work was scanned for this document. It is handwritten but nearly all legible.

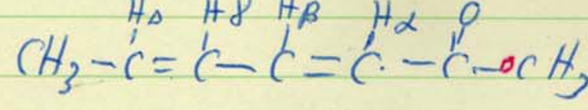
simpler indicating that less cis isomer present here than in other compound from other preparation.

4/6/73 0.1g methyl sorbate (Prep 71) dissolved in .5cc CCl_4 with

n.m.r. #50 several drops CH_2Cl_2 internal standard. n.m.r. taken. Eu resolve II added in increments and shifts noted

50a	30 mg. added	some shift noted
50b	60 " "	considerable shifting former 1H multiplet now d of d
50c	100 "	" d of d and a clean doublet now visible
50d	140 "	" as above but methoxy now shifted into 2H multiplet

4/7/73	50e	200 "	" OCH_3 shifting out of 2H multiplet.
	50f	250 "	" 2H multiplet resolving into doublet of doublets and
	50g	300 "	" all protons now separated!! (Glen Rake)



$J\alpha\beta = 16$ cps $= J\beta\alpha$
$J\beta\gamma = 10$ cps $= J\gamma\beta$
$J\gamma\Delta = 15$ cps $= J\Delta\gamma$
$J\Delta{-}CH_3 = 6$ cps $= JCH_3{-}\Delta$.

4/9/73 The Europium shift data obtained above was placed in tabular and graphical form. The data are summarized on the next four pages

Methyl Sorbate Eu resolve Exp.

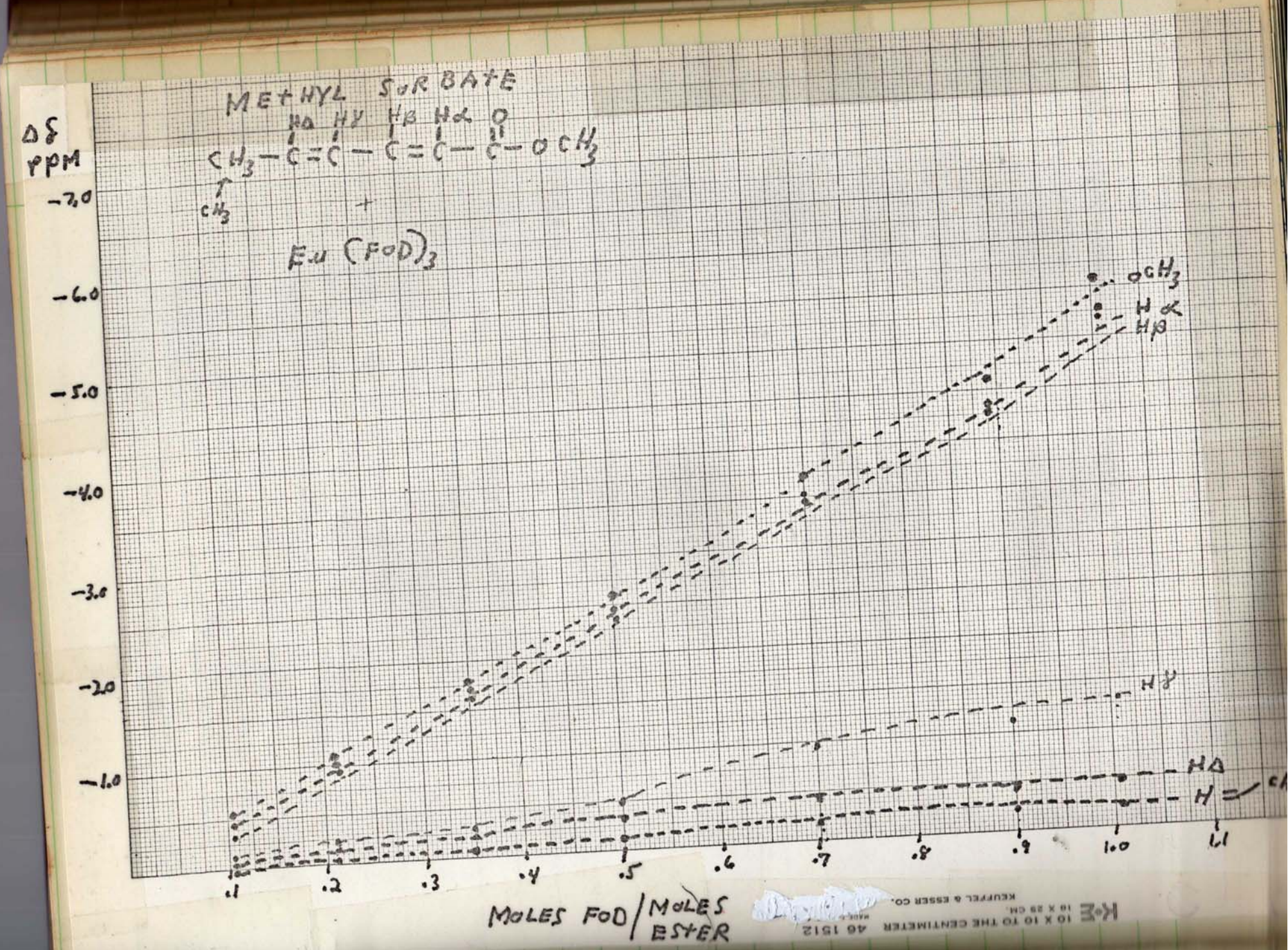
a) Assumes 3 ligands in mole complex
* Relative to internal CH_2Cl_2

1

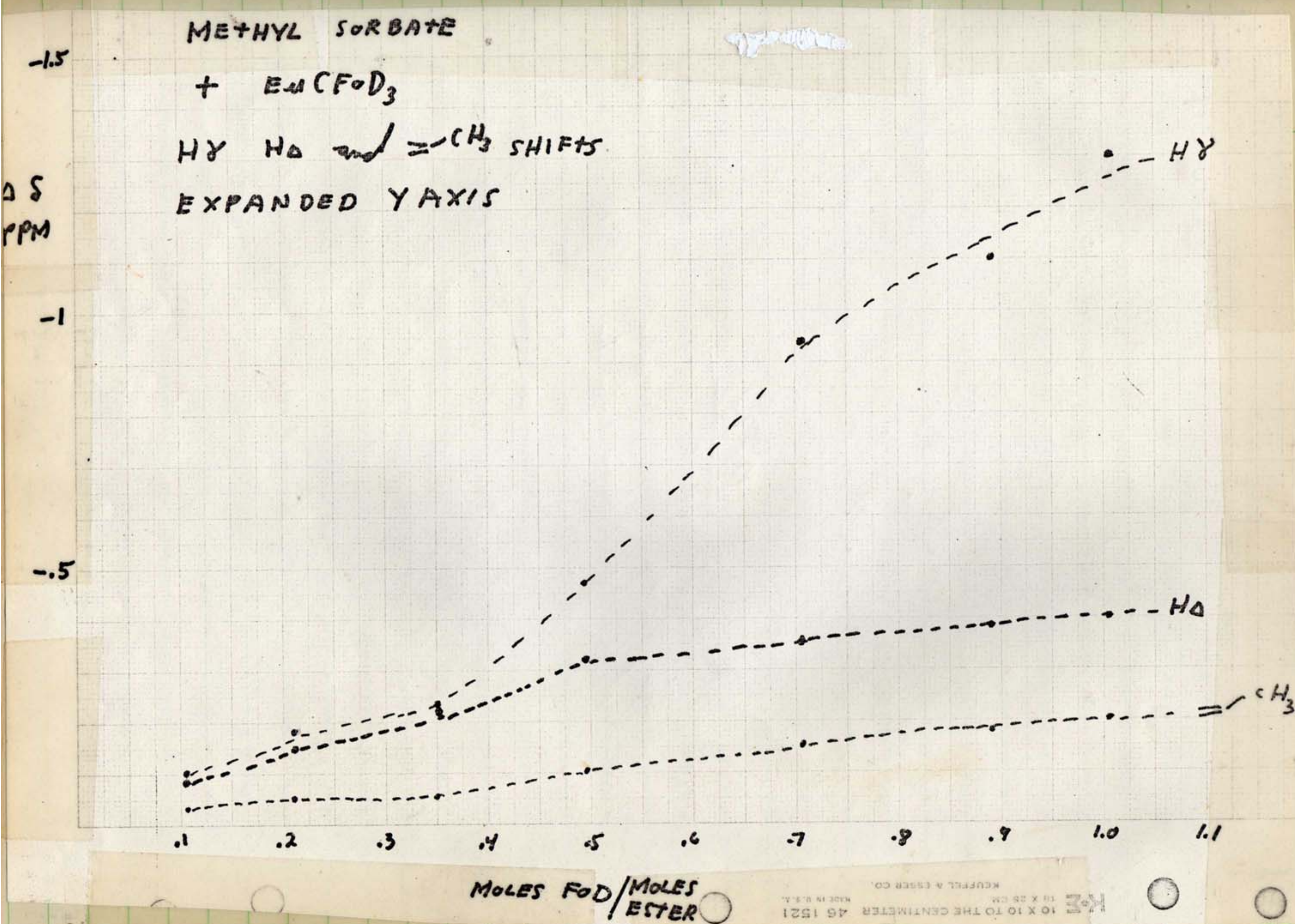
POD/ESTER a	Hz Obsv.*	Hz Orig.*	Δ Hz	Δ δ PPM	Δ (Δ δ PPM)
		OCH_2			
0.00	+100	+100	0	0	0
0.10	+66	"	-34	-.6	—
0.21	+35	"	-65	-1.1	-.5
0.35	-8	"	-108	-1.8	-.7
0.50	-57	"	-157	-2.6	-.8
0.70	-117	"	-217	-3.7	-1.1
0.89	-177	"	-277	-4.6	-.9
1.06	-239	"	-339	-5.6	-1.0
		$H\alpha$			
0.00	-23	-23	0	0	0
0.10	-55	"	-32	-.54	—
0.21	-87	"	-64	-1.9	-.53
0.35	-126	"	-103	-1.72	-.65
0.50	-169	"	-146	-2.44	-.72
0.70	-230	"	-207	-3.45	-1.01
0.89	-285	"	-262	-4.37	-.92
1.06	-344	"	-321	-5.35	-.98
		$H\beta$			
0.00	-111	-111	0	0	0
0.10	-131	"	-20	-.33	—
0.21	-174	"	-63	-1.05	-.72
0.35	-214	"	-103	-1.72	-.67
0.50	-256	"	-145	-2.46	-.70
0.70	-320	"	-209	-3.49	-1.07
0.89	-372	"	-261	-4.36	-.87
1.06	-427	"	-316	-5.27	-.91

c) assuming 3 ligands per mole complex * rel. to water

FOD/ESTER	Hz Obsv.*	Hz calc.*	ΔHz	ΔPPM	Δ(ΔPPM)
		HY			
0.00	-49	-49	0	0	0
0.10	-55	"	-6	-.100	—
0.21	-60	"	-11	-.183	-.083
0.35	-63	"	-14	-.234	-.051
0.50	-87	"	-28	-.470	-.236
0.70	-105	"	-56	-.940	-.470
0.89	-115	"	-66	-1.10	-.160
1.06	-128	"	-79	-1.30	-.200
		HΔ			
0.00	-49	-49	0	0	0
0.10	-55	"	-6	-.1	—
0.21	-58	"	-9	-.15	-.05
0.35	-63	"	-14	-.234	-.18
0.50	-68	"	-19	-.32	-.09
0.70	-70	"	-21	-.35	-.03
0.89	-72	"	-23	-.38	-.03
1.06	-73	"	-24	-.40	-.02
		$=/CH_3$			
0.00	+210	+210	0	0	0
0.10	+208	"	-2	-.03	—
0.21	+207	"	-3	-.05	-.02
0.35	+207	"	-3	-.05	0.00
0.50	+204	"	-6	-.10	-.05
0.70	+201	"	-9	-.15	-.05
0.89	+199	"	-11	-.18	-.03
1.06	+198	"	-12	-.20	-.02


METHYL SORBATE
Hδ Hγ Hβ Hα O
CH3 – C = C – C = C – C – OCH3
CH3
+
Eu (FOD)3
Δδ ppm
-7.0
-6.0
-5.0
-4.0
-3.0
-2.0
-1.0
OCH3
Hα
Hβ
Hγ
Hδ
H
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
1.1
MOLES FOD / MOLES ESTER

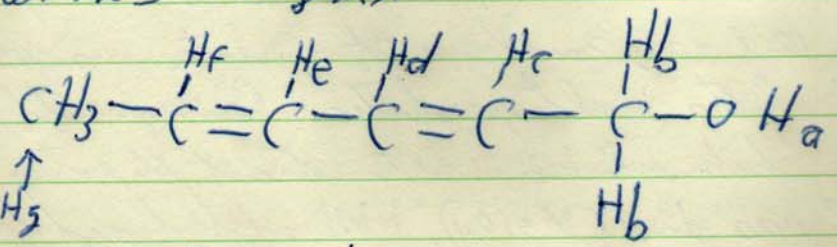
MOLES FOD / MOLES ESTER



5/2/73 I.R. and n.m.r. spectra taken on commercial (absolute)
n.m.r. #68 salyl alcohol. Material believed pure enough to
I.R. #180 undertake shift reagent study.

n.m.r. #69 routine salyl alcohol spectrum, CH_2I standard
69a 100 Mg alcohol, 50 mg $Cu(CF_3CO_2)_2$
69b " " 100 " " "
69c " " 150 " " "
69d " " 200 " " "
69e " " 250 " " "
69f " " 300 " " "
69g " " 350 " " "
69h " " 450 " " "
69i " " 550 " " " Now all protons titrated
5/3/73 69j " " 700 " " Completely separated, titrated
69k " " " " " Protons blown up

Study indicates a second isomer in addition to the all trans (second doublet in CH_3 region).



$J_{ab} = J_{ba} = 0$
$J_{bc} = J_{cb} = 5\,Hz$
$J_{cd} = J_{dc} = 14\,Hz$
$J_{de} = J_{ed} = 9\,Hz$
$J_{ef} = J_{fe} = 14\,Hz$
$J_{fg} = J_{gf} = 5.5\,Hz$

The data was put in Tabular and graphical form (20 [illegible]

Eu(FOD)$_3$ titrated with ORBOYL ALCOHOL

Eu / ALC	H_2 obsvd*	H_3 org.	ΔH_2	$\Delta\delta$ PPM	$\Delta(\Delta\delta$ PPM)
0.00	−97	−97	0	0	0
0.046	−359	−97	−262	−4.37	0
0.0915	−594	−97	−497	−8.30	−3.93
0.137	−840	−97	−743	−12.35	−4.05
0.183	−1103	−97	−1006	−16.67	−4.32
0.229	−1360	−97	−1263	−21.00	−4.33
			H_b	H_3C-O	
0.00	−109	−109	0	0	0
0.046	−175	−109	−66	−1.1	0.00
0.0915	−232	−109	−123	−2.0	−0.90
0.137	−297	−109	−188	−3.14	−1.14
0.183	−355	−109	−246	−4.10	−0.96
0.229	−424	−109	−315	−5.25	−1.15
0.274	−492	−109	−383	−6.40	−1.15
0.320	−562	−109	−453	−7.55	−1.15
0.412	−707	−109	−598	−10.00	−2.45
0.515	−798	−109	−689	−11.50	−1.50
0.640	−859	−109	−750	−12.50	−1.00
0.00	−213	−213	0 H_5	0	0
0.046	−245	−213	−32	−.54	0
0.0915	−285	−213	−72	−1.20	−0.66
0.137	−333	−213	−120	−2.0	−0.80
0.183	−355	−213	−142	−2.37	−0.37
0.229	−392	−213	−179	−3.0	−0.63
0.274	−430	−213	−217	−3.62	−0.62
0.320	−470	−213	−257	−4.30	−0.68
0.412	−540	−213	−327	−5.45	−1.15
0.515	−593	−213	−380	−6.35	−0.90
0.640	−620	−213	−407	−6.80	−0.45

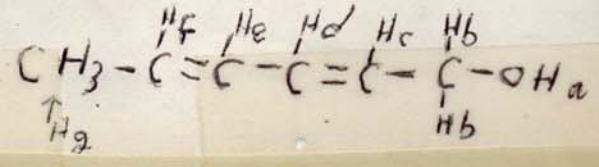
* = Rel to internal H_2I

Hd

Eu / Alcohol	H2 Obsvs.	H2 avg.	ΔH2	Δδ PPM	Δ(Δδ PPM)
0.00	−213	−213	0	0	0
0.046	−245	−213	−32	−0.54	0
0.0915	−285	−213	−72	−1.16	−0.62
0.137	−313	−213	−100	−1.67	−0.51
0.183	−350	−213	−137	−2.28	−0.61
0.229	−382	−213	−169	−2.82	−0.54
0.274	−420	−213	−207	−3.45	−0.63
0.320	−458	−213	−245	−4.16	−0.65
0.412	−524	−213	−311	−5.20	−1.10
0.515	−557	−213	−344	−5.74	−0.54
0.640	−575	−213	−362	−6.03	−0.29

He

0.00	−213	−213	0	0	0
0.046	−235	−213	−22	−0.37	0
0.0915	−245	−213	−32	−0.54	−0.17
0.137	−260	−213	−47	−0.79	−0.25
0.183	−275	−213	−62	−1.03	−0.24
0.229	−285	−213	−72	−1.20	−0.17
0.274	−297	−213	−84	−1.40	−0.20
0.320	−310	−213	−97	−1.62	−0.22
0.412	−330	−213	−117	−1.95	−0.33
0.515	−347	−213	−127	−2.12	−0.17
0.640	−353	−213	−140	−2.34	−0.22

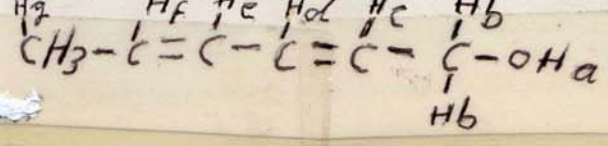


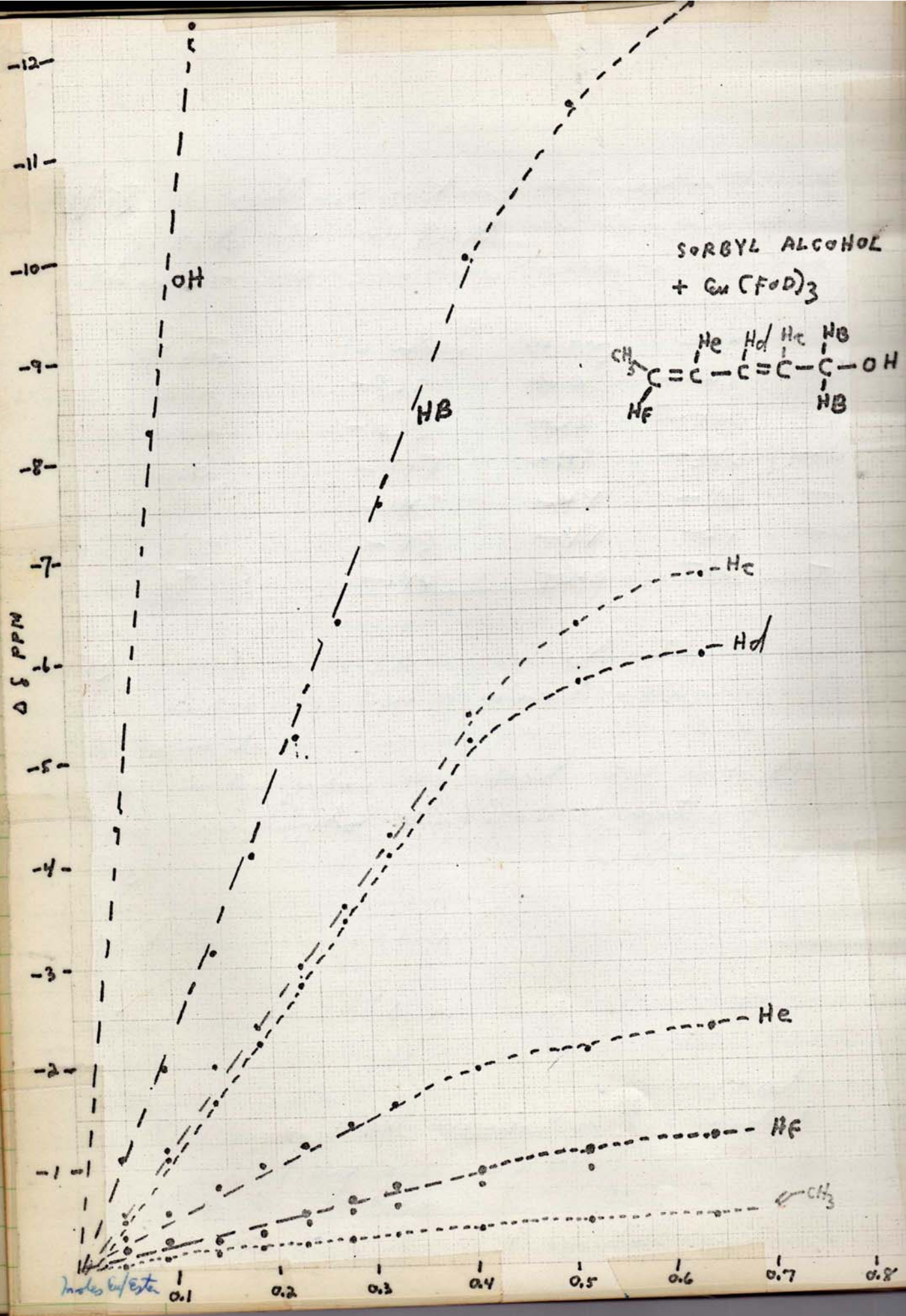
H_F

Eu / Alcohol	Hz Observ.	Hz ORIG.	Δ Hz	Δ δ PPM	Δ (Δ δ PPM)
0.00	−213	−213	0	0	0
0.046	−230	−213	−17	−0.284	0
0.0915	−231	−213	−18	−0.30	−0.016
0.137	−231	−213	−18	−0.30	0
0.183	−240	−213	−27	−0.45	0.150
0.229	−245	−213	−32	−0.54	0.090
0.274	−250	−213	−37	−0.62	0.080
0.320	−262	−213	−49	−0.82	0.20
0.412	−270	−213	−57	−0.95	0.13
0.515	−283	−213	−70	−1.17	0.22
0.640	−287	−213	−74	−1.24	0.07

H_a

0.00	+22	+22	0	0	0
0.046	+18	+22	−4	−0.067	0
0.0915	+15	+22	−7	−0.117	−0.050
0.137	+13	+22	−9	−0.150	−0.033
0.183	+11	+22	−11	−0.183	−0.033
0.229	+9	+22	−13	−0.217	−0.034
0.274	+6	+22	−16	−0.277	−0.060
0.320	+3	+22	−19	−0.317	−0.040
0.412	0	+22	−22	−0.370	−0.053
0.515	−2	+22	−24	−0.400	−0.030
0.640	−4	+22	−26	−0.434	−0.034




SORBYL ALCOHOL
+ Eu(FOD)3
OH
HB
Hc
Hd
He
Hf
CH3
Δδ PPM
-12
-11
-10
-9
-8
-7
-6
-5
-4
-3
-2
-1
Moles Eu/Ester
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8

Benzyl alcohol + $Eu(FOD)_3$ STUDY

* rel. to internal CH_2Cl_2

OH

Eu/alc.	Hz obsvd.*	Hz orig.*	Δ Hz	Δ δ PPM	Δ (Δ δ PPM)
0.00	+86	+86	0	0	0
0.084	−322	+86	−408	−6.8	−6.8
0.168	−757	+86	−843	−14.0	−7.2

H Benzylic

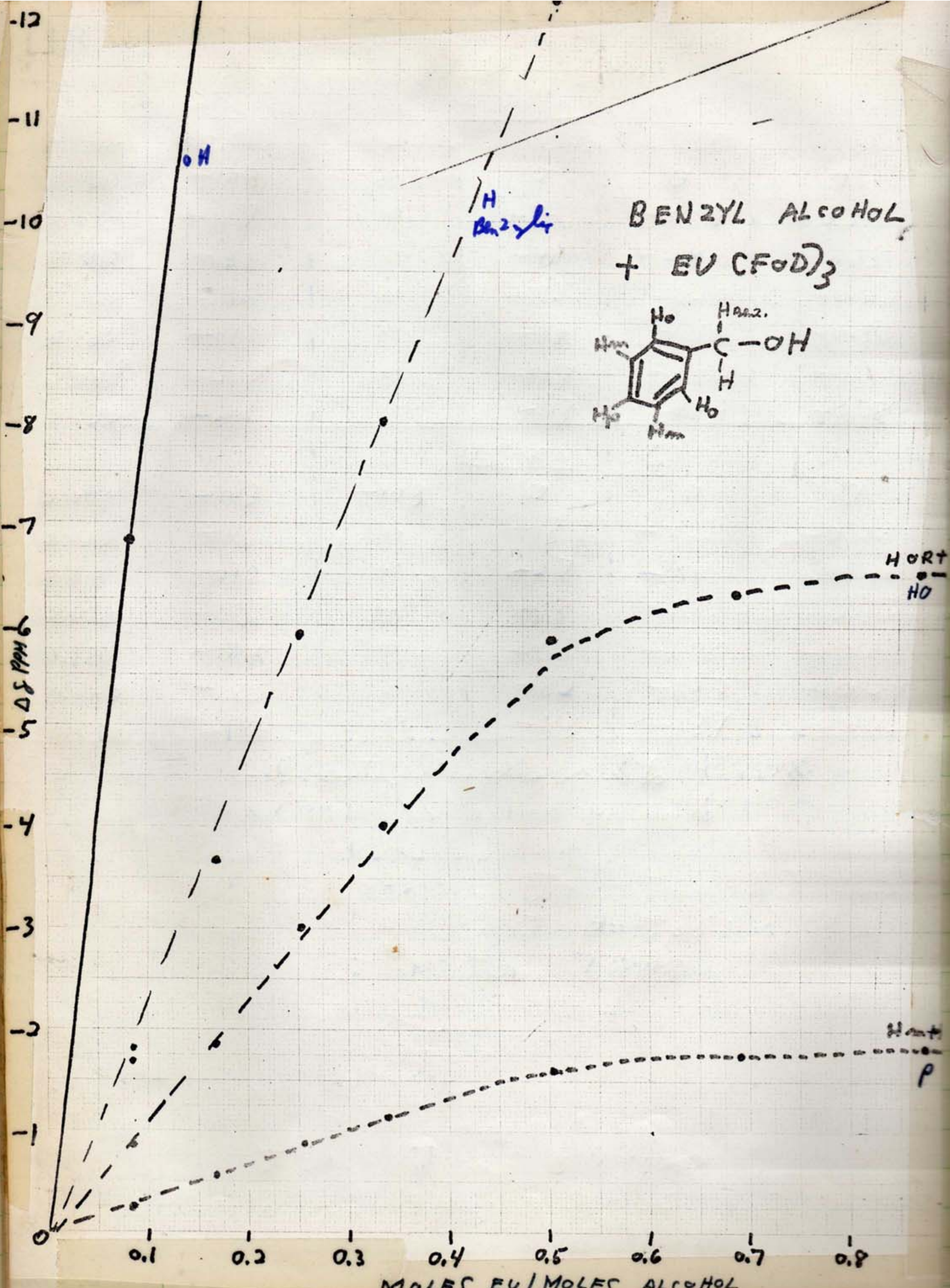
0.00	+44	+44	0	0	0
0.084	−58	+44	−102	−1.70	−1.70
0.168	−176	+44	−220	−3.67	−1.97
0.252	−309	+44	−353	−5.89	−2.22
0.336	−437	+44	−481	−8.02	−2.13
0.508	−687	+44	−731	−12.20	−4.18
0.690	−769	+44	−813	−13.54	−1.34
0.875	−803	+44	−847	−14.10	−0.56

H ORTHO

0.00	−124	−124	0	0	0
0.084	−175	−124	−51	−0.85	−0.85
0.168	−235	−124	−111	−1.85	−1.00
0.252	−305	−124	−181	−3.02	−1.17
0.336	−365	−124	−241	−4.02	−1.00
0.508	−476	−124	−352	−5.87	−1.85
0.690	−503	−124	−379	−6.32	−0.45
0.875	−516	−124	−392	−6.54	−0.22

H m + p

0.000	−124	−124	0	0	0
0.084	−139	−124	−15	−0.25	−0.250
0.168	−156	−124	−32	−0.534	−0.284
0.252	−177	−124	−53	−0.883	−0.349
0.336	−192	−124	−68	−1.135	−0.252
0.508	−220	−124	−96	−1.600	−0.465
0.690	−228	−124	−104	−1.740	−0.140
0.875	−231	−124	−107	−1.780	−0.040



BENZYL ALCOHOL
+ EU (FOD)3
OH
H Benzylic
H ORT
HO
H m+
P
Δδ PPM
MOLES EU / MOLES ALCOHOL
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
-11
-12

5/15/73 $Eu(FOD)_3$ experiments were begun with phenol.
n.m.r. #72 Routine Spectrum 80 Mg ΦOH, CCl_4 soln, CH_2Cl_2 standard
" 72a 80 Mg ΦOH + 50 Mg $Eu(FOD)_3$. Hortho separated to doublet
72b " " " +100 " " as above.
72c " " " +200 " " H m + p now clean 6 line pattern.

5/16/73 72d " " " +300 " " H m and p now separating
72e " " " +400 " " H m and p now distorted triplets
5/17/73 72f " " " 500 " " Poor spectrum now due to viscosity

Data put in tabular form

ΦOH + $Eu(FOD)_3$

* rel. internal CH_2Cl_2

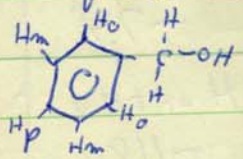
Eu/alc.	H_2 obsvd.*	ΦH H_2 orig.*	ΔH_2	$\Delta\delta$ PPM	$\Delta(\Delta\delta$PPM)
0.00	−74	−74	0	0	0
0.055	−415	−74	−341	−5.70	−5.70
0.110	−721	−74	−647	−10.8	−5.10
0.220	−1268	−74	−1194	−19.9	−9.1
		Hortho			
0.000	−118	−118	0	0	0
0.055	−164	−118	−46	−0.77	−0.77
0.118	−218	−118	−100	−1.67	−0.90
0.220	−315	−118	−197	−3.28	−1.61
0.330	−393	−118	−275	−4.60	−1.32
0.440	−462	−118	−344	−5.74	−1.14
0.550	−485	−118	−367	−6.10	−0.36

phenol + $Eu(FOD)_3$

H META

Eu/alc.	Hz observ.	Hz orig.	ΔHz	Δ δ PPM	Δ (Δ δ PPM)
0.000	−103	−103	0	0	0
0.055	−137	"	−34	−0.57	−0.57
0.110	−151	"	−48	−0.80	−0.23
0.220	−175	"	−72	−1.20	−0.40
0.330	−193	"	−90	−1.50	−0.30
0.440	−210	"	−107	−1.80	−0.30
0.550	−216	"	−113	−1.88	−0.08
			H PARA		
0.000	−103	−103	0	0	0
0.055	−116	"	−13	−0.22	−0.22
0.110	−130	"	−27	−0.45	−0.23
0.220	−152	"	−49	−0.82	−0.37
0.330	−168	"	−65	−1.08	−0.26
0.440	−185	"	−82	−1.37	−0.29
0.550	−186	"	−83	−1.39	−0.02

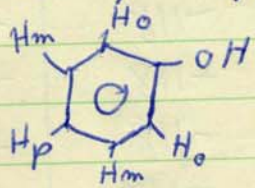
Calculations of Coupling Constants Obtained for ϕCH_2OH and ϕOH from $Eu(FOD)_3$ experiments



$J_{om} = J_{mo} = 7.0$ cps

$J_{op} = J_{po} = 2.5$ cps

$J_{mp} = J_{pm} = 7$ cps.

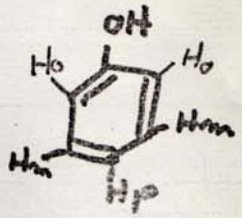


$J_{om} = J_{mo} = 8.0$ cps

$J_{op} = J_{po} = 1.5$ cps

$J_{mp} = J_{pm} = 7.5$ cps

ΦOH + Eu(FOD)$_3$


OH
Ho
Ho
Hm
Hm
Hp

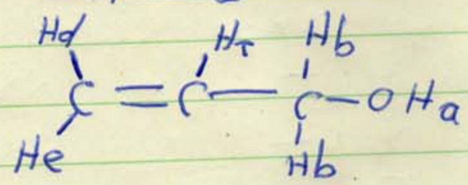
OH
-10.0
-9.0
-8.0
-7.0
-6.0
-5.0
-4.0
-3.0
-2.0
-1.0
Δδ PPM
H ORTHO
H META
H PARA
0.1
0.2
0.3
0.4
0.5
0.6
0.7
MOLES EU/MOLES ΦOH

Eu(FOD)$_3$ Studies with allyl alcohol

5/18/73
N. M. R.

# 73a	Routine Spectrum 55 Mg allyl alcohol + .5 ml CCl_4 + CH_3I standard
73b	55 Mg allyl alcohol + 50 Mg Eu(FOD)$_3$
73c	" " " " + 100 " "
73d	" " " " - 150 " "
73e	" " " " 200 " " Spectrum now shorter
73f	" " " " 250 " " "
73g	" " " " 300 " " "

Coupling Constants for allyl alcohol

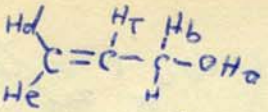


J_{ab} = 5.5 cps = J_{ba} (seen only in conc. solution, decouples with Eu).
J_{bc} = 5 cps = J_{cb}
J_{dc} = 11 cps = J_{cd}
J_{ce} = 17.5 cps = J_{ec}
J_{de} = 1.5 cps = J_{ed}
J_{bd} = J_{db} = J_{be} = J_{eb} ≅ 1 cps

Eu/alc Ratios for allyl alcohol study above

50 Mg = .0492
100 Mg = .0984
150 Mg = .1476
200 Mg = .1968
250 Mg = .2460
300 Mg = .2952

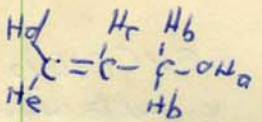
The data was tabulated
see opp page.



ALLYL ALCOHOL + EU(FOD)$_3$

* rel. to internal CH_3I

EU/ALC.	HZ OBS.*	HZ ORIG.*	OH ΔHZ	Δ PPM	Δ(Δ δ PPM
0.000	−124	−124	0	0	0
0.049	−410	"	−286	−4.77	−4.77
0.098	−727	"	−603	−10.00	−5.23
0.148	−1030	"	−906	−15.1	−5.10
0.000	−124	−124	Hb 0	0	0
0.049	−191	"	−67	−1.12	−1.12
0.098	−275	"	−151	−2.52	−1.40
0.148	−353	"	−229	−3.82	−1.30
0.197	−433	"	−309	−5.15	−1.33
0.246	−518	"	−394	−6.57	−1.42
0.295	−620	"	−496	−8.27	−1.50
0.000	−229	−229	Hτ 0	0	0
0.049	−272	"	−43	−0.72	−0.72
0.098	−317	"	−88	−1.47	−0.75
0.148	−361	"	−132	−2.20	−0.73
0.197	−405	"	−176	−2.94	−0.74
0.246	−451	"	−222	−3.70	−0.76
0.295	−504	"	−275	−4.58	−0.88
			Hd		
0.000	−187	−187	0	0	0
0.049	−197	"	−10	−0.17	−0.17
0.098	−225	"	−38	−0.64	−0.47
0.148	−249	"	−62	−1.03	−0.39
0.197	−272	"	−85	−1.42	−0.39
0.246	−297	"	−110	−1.84	−0.42
0.295	−327	"	−140	−2.33	−0.49



ALLYL ALCOHOL + Eu(FOD)$_3$ (Continued)

* Rel. internal CH$_2$I

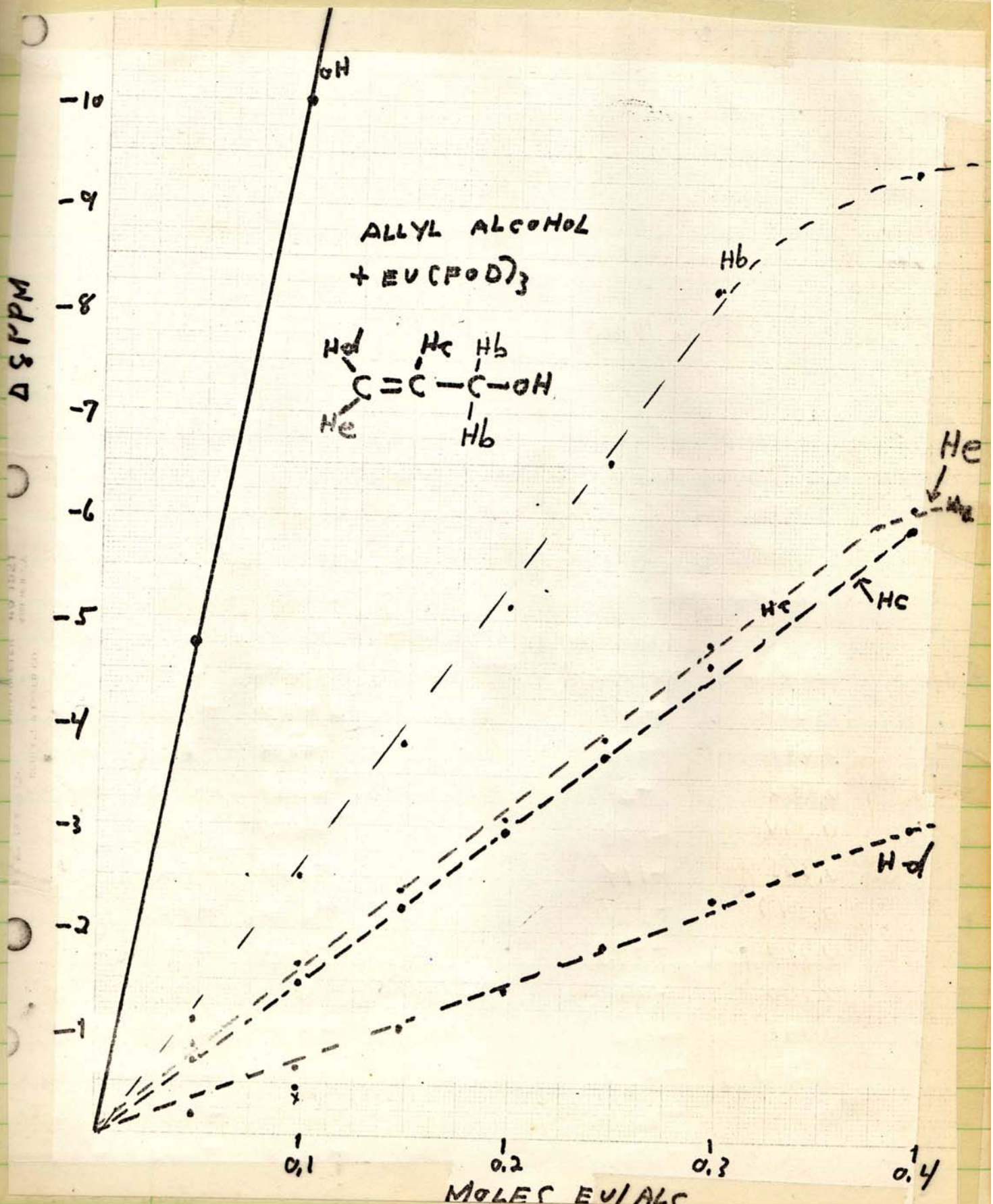
Eu/alc.	H2 obsvd.*	H2 orig.* (He)	ΔHz	ΔPPM	Δ(ΔPPM)
0.000	−174	−174	0	0	0
0.049	−224	"	−50	−0.84	−0.84
0.098	−273	"	−99	−1.65	−0.81
0.148	−316	"	−142	−2.37	−0.72
0.197	−359	"	−185	−3.08	−0.71
0.246	−406	"	−232	−3.87	−0.79
0.295	−461	"	−287	−4.79	−0.92

ΔPPM

5/21/73 An additional point was taken. 55 MΣ allyl alcohol + 400 MΣ Eu FOD
N.M.R.#732 Eu/alc = 0.392

Proton	Hz obsvd.	Hz orig.	ΔHz.	ΔPPM
Hb	−688	−124	−564	−9.4
Hc	−587	−229	−358	−5.97
Hd	−370	−187	−183	−3.05
He	−542	−174	−368	−6.15

the data was put in graphical form.
(See opp. page.)


ALLYL ALCOHOL
+ EU(FOD)3
Ha Hc Hb
C=C—C—OH
He Hb
OH
Hb
He
Hc
Hc
Ha
Δ δ PPM
-10
-9
-8
-7
-6
-5
-4
-3
-2
-1
0.1
0.2
0.3
0.4
MOLES EU/ALC

5/22/73 Eu(Fod)$_3$ shift studies undertaken with $\Phi-C=C-\overset{O}{\overset{\|}{C}}-CH_3$.

n.m.r. #74 75 Mg $\Phi-\overset{H_b}{C}=\overset{H_a}{C}-\overset{O}{\overset{\|}{C}}-CH_3$ + CCl_4 + CH_2Cl_2. Routine Spectrum

74a " " " + 50 Mg Eu(FOD)$_3$.

74b " " " + 100 Mg "

74c " " " 150 Mg "

74d " " " 200 Mg "

74e " " " + 300 Mg "

74f " " " + 400 Mg "

during the addition H_a gradually overtook H_b resulting in a two proton AB pattern (74b), a sharp two proton singlet (74c), and then passed it AB pattern (74d), doublets of doublets (74e and f). H ortho separated readily (74c and thereafter). The data was tabulated and graphed.

Eu(FOD)$_3$ + $\Phi-\overset{H_b}{C}=\overset{H_a}{C}-\overset{O}{\overset{\|}{C}}-CH_3$ * rel. internal CH_2Cl_2

5/23/73

Eu/ketone	Hz obsv.*	$\underline{CH_3}$ Hz orig.*	ΔHz	ΔPPM	Δ(S)PPM
0.000	+181	+181	0	0	0
0.091	+94	"	-87	-1.45	-1.45
0.182	-2	"	-183	-3.05	-1.60
0.274	-103	"	-284	-4.74	-1.69
0.365	-199	"	-380	-6.35	-1.61
0.547	-361	"	-542	-9.03	-2.68
0.730	-443	"	-624	-10.40	-1.37
0.000	-79	$\underline{H_a}$ -79	0	0	0
0.091	-162	"	-83	-1.38	-1.38
0.182	-252	"	-173	-2.88	-1.50
0.274	-353	"	-274	-4.57	-1.69
0.365	-446	"	-367	-6.12	-1.55
0.547	-590	"	-511	-8.55	-2.43
0.730	-656	"	-577	-9.61	-1.06

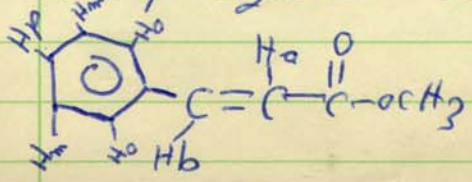
$\phi-\underset{H_b}{C}=\underset{H_a}{C}-\overset{O}{\overset{\|}{C}}-CH_3$ + Eu(FOD)$_3$ (Cont.)

* pel. internal CH_2Cl_2

Eu/Ketone	Hz obsvd*	Hz orig.*	ΔHz	Δ PPM	Δ(δ PPM)
		Hb			
0.000	−129	−129	0	0	0
0.091	−197	"	−68	−1.13	−1.13
0.182	−274	"	−145	−2.42	−1.29
0.274	−353	"	−224	−3.74	−1.32
0.365	−422	"	−293	−4.89	−1.15
0.547	−549	"	−420	−7.00	−2.11
0.730	−612	"	−483	−8.05	−1.05
		H ORTHO			
0.000	−124	−124	0	0	0
0.091	−146	"	−22	−0.37	−0.37
0.182	−165	"	−41	−0.69	−0.32
0.274	−181	"	−57	−0.95	−0.26
0.365	−198	"	−74	−1.23	−0.28
0.547	−221	"	−97	−1.62	−0.29
0.730	−231	"	−107	−1.78	−0.16
		H m+p			
0.000	−124	−124	0	0	0
0.091	−128	"	−4	−0.07	−0.07
0.182	−132	"	−8	−0.13	−0.06
0.274	−139	"	−15	−0.25	−0.12
0.365	−146	"	−22	−0.37	−0.12
0.547	−154	"	−30	−0.50	−0.13
0.730	−157	"	−33	−0.55	−0.05

CH_2Cl_2 Δ(δ PPM)
0
1.45
1.60
1.69
1.61
0.68
1.37
0
1.38
1.50
1.69
1.55
2.43
1.06

Coupling Constants for $\phi-C=C-\overset{O}{\overset{\|}{C}}-CH_3$

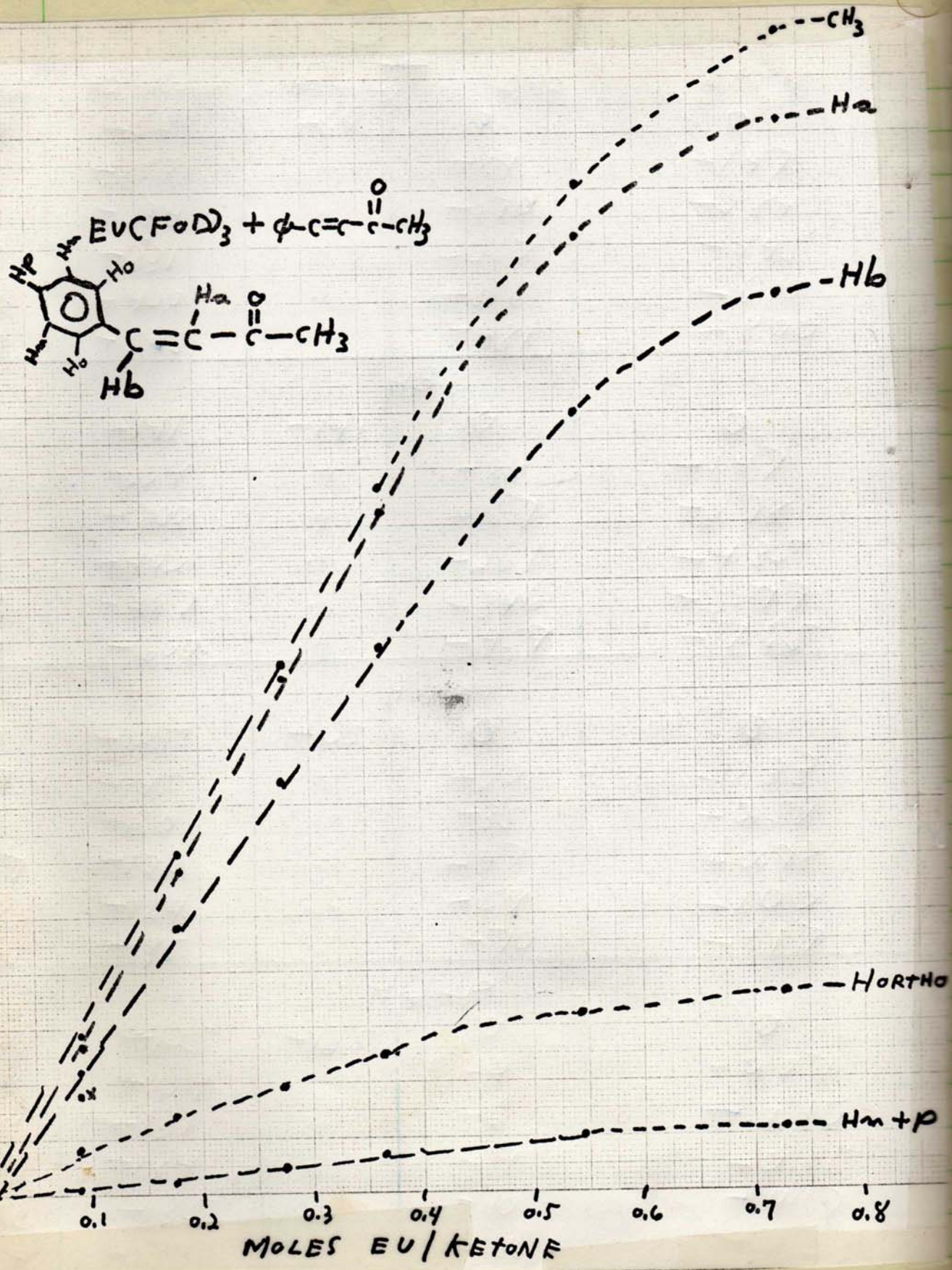


$J_{ab} = J_{ba} = 16$ cps

$J_{om} = J_{mo} = 7.5$ cps

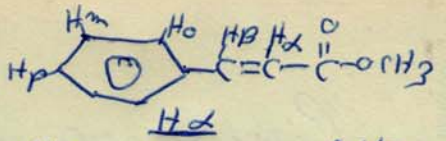
$J_{op} = J_{po} = 2.0$ cps

$J_{mp} = J_{pm} = 7.5$ cps

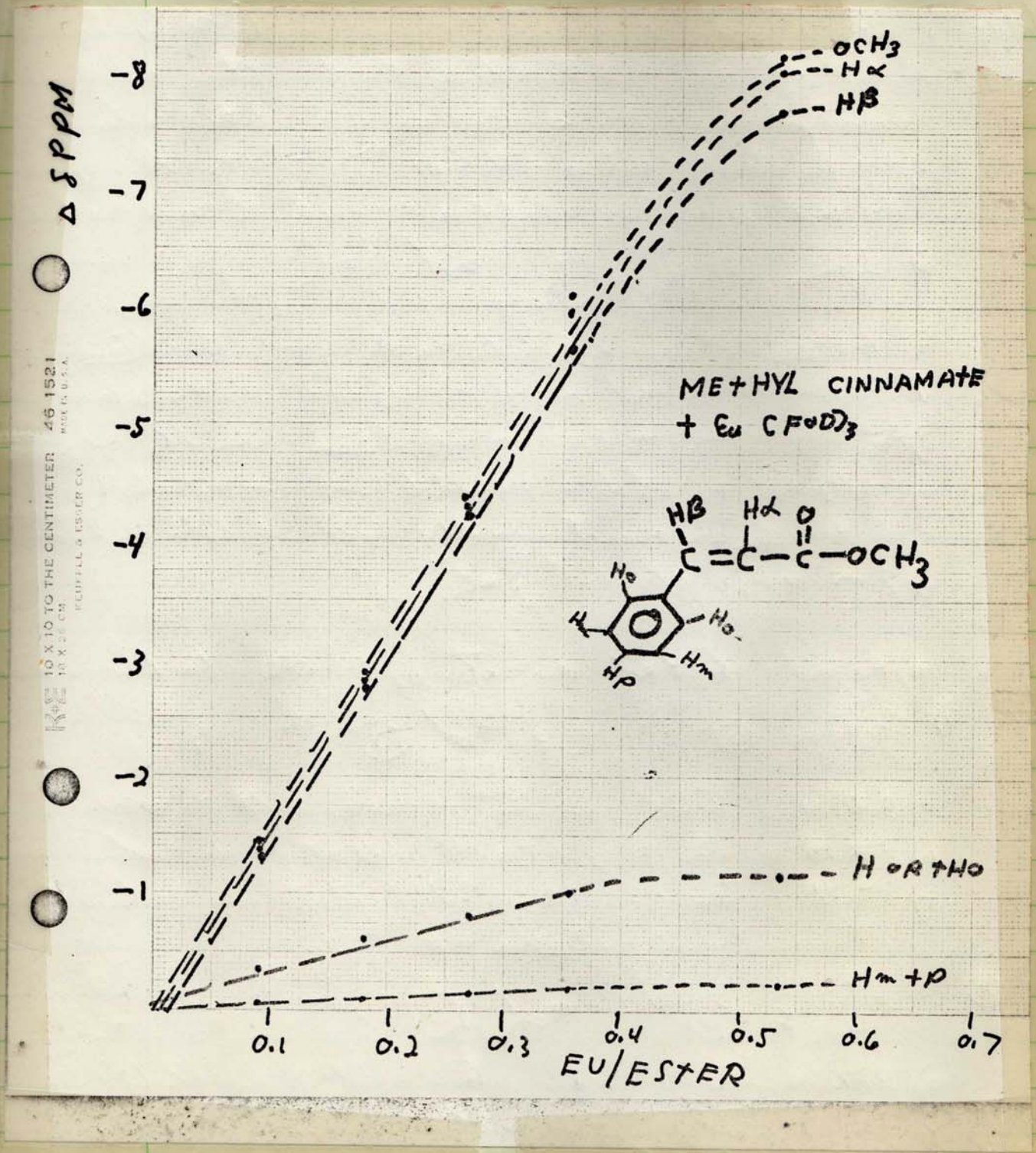

$EuCFoD)_3 + \phi-C=C-\overset{O}{\overset{\|}{C}}-CH_3$
Ha
Hb
Ho
Hm
Hp
$\overset{Ha}{\underset{Hb}{C}}=C-\overset{O}{\overset{\|}{C}}-CH_3$
-CH3
Ha
Hb
HORTHO
Hm+p
Δδ ppm
-10
-9
-8
-7
-6
-5
-4
-3
-2
-1
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
MOLES EU / KETONE

Eq/Este	Hz observ.*		ΔHz	−ΔPPM
0.000	+92	+92	0	0
0.089	+5	"	−87	−1.45
0.178	−77	"	−169	−2.82
0.267	−173	"	−265	−4.42
0.356	−264	"	−356	−5.95
0.534	−397	"	−489	−8.16

* = rel. interval CH_3 (Hz)



Eu/ester	H2 obsvn	H2 orig.	ΔH2	ΔPPM
0.000	−64	−64	0	0
0.089	−153	"	−89	−1.47
0.178	−234	"	−170	−2.84
0.267	−331	"	−267	−4.45
0.356	−420	"	−356	−6.10
0.534	−545	"	−481	−8.00
		Hβ		
0.000	−141	−141	0	0
0.089	−229	"	−88	−1.47
0.178	−308	"	−167	−2.78
0.267	−402	"	−261	−4.35
0.356	−487	"	−346	−5.77
0.534	−600	"	−459	−7.65
		Hortho		
0.000	−125	−125	0	0
0.089	−145	"	−20	−0.33
0.178	−160	"	−35	−0.59
0.267	−172	"	−47	−0.78
0.356	−184	"	−59	−1.00
0.534	−195	"	−70	−1.17
		Hm+p		
0.000	−125	−125	0	0
0.089	−129	"	−4	−0.07
0.178	−131	"	−6	−0.10
0.267	−134	"	−9	−0.15
0.356	−135	"	−10	−0.17
0.534	−139	"	−14	−0.23


Δ δ PPM
-8
-7
-6
-5
-4
-3
-2
-1
OCH3
Hα
Hβ
METHYL CINNAMATE
+ Eu CF₃OD)₃
Hβ
Hα
O
C=C-C-OCH3
Ho
Hm
Hp
H ORTHO
Hm+p
0.1
0.2
0.3
0.4
0.5
0.6
0.7
EU/ESTER

$Eu(FOD)_3$ + Geraniol (Contd) * Rel. internal CH_2Br_2

* $C=C-CH_2OH$ (HK)

Eu/alc.	H_2 obsvd *	H_2 irrad.	ΔH_2	Δ PPM	Δ SPPM
0.00	−21	−21	0	0	0
0.09	−107	"	−86	−1.43	−1.43
0.18	−192	"	−171	−2.85	−1.42
0.27	−279	"	−258	−4.30	−1.45
0.36	−350	"	−329	−5.50	−1.20
0.45	−419	"	−398	−6.65	−1.15
0.54	−460	"	−439	−7.32	−0.67
0.63	−480	"	−459	−7.65	−0.33
		INTERNAL METHYL			
0.00	+200	+200	0	0	0
0.09	+163	"	−37	−0.62	−0.62
0.18	+132	"	−68	−1.13	−0.51
0.27	+95	"	−105	−1.75	−0.62
0.36	+63	"	−137	−2.29	−0.54
0.45	+34	"	−166	−2.77	−0.48
0.54	+17	"	−183	−3.05	−0.28
0.63	+9	"	−191	−3.18	−0.13
		CH_3-CH_2			
0.00	+172	+172	0	0	0
0.09	+154	"	−18	−0.30	−0.30
0.18	+138	"	−34	−0.57	−0.27
0.27	+116	"	−56	−0.94	−0.37
0.36	+99	"	−73	−1.22	−0.28
0.45	+84	"	−88	−1.47	−0.25
0.54	+76	"	−96	−1.60	−0.13
0.63	+72	"	−100	−1.67	−0.07

Eu(FOD)$_3$ + Geraniol (Contd.)

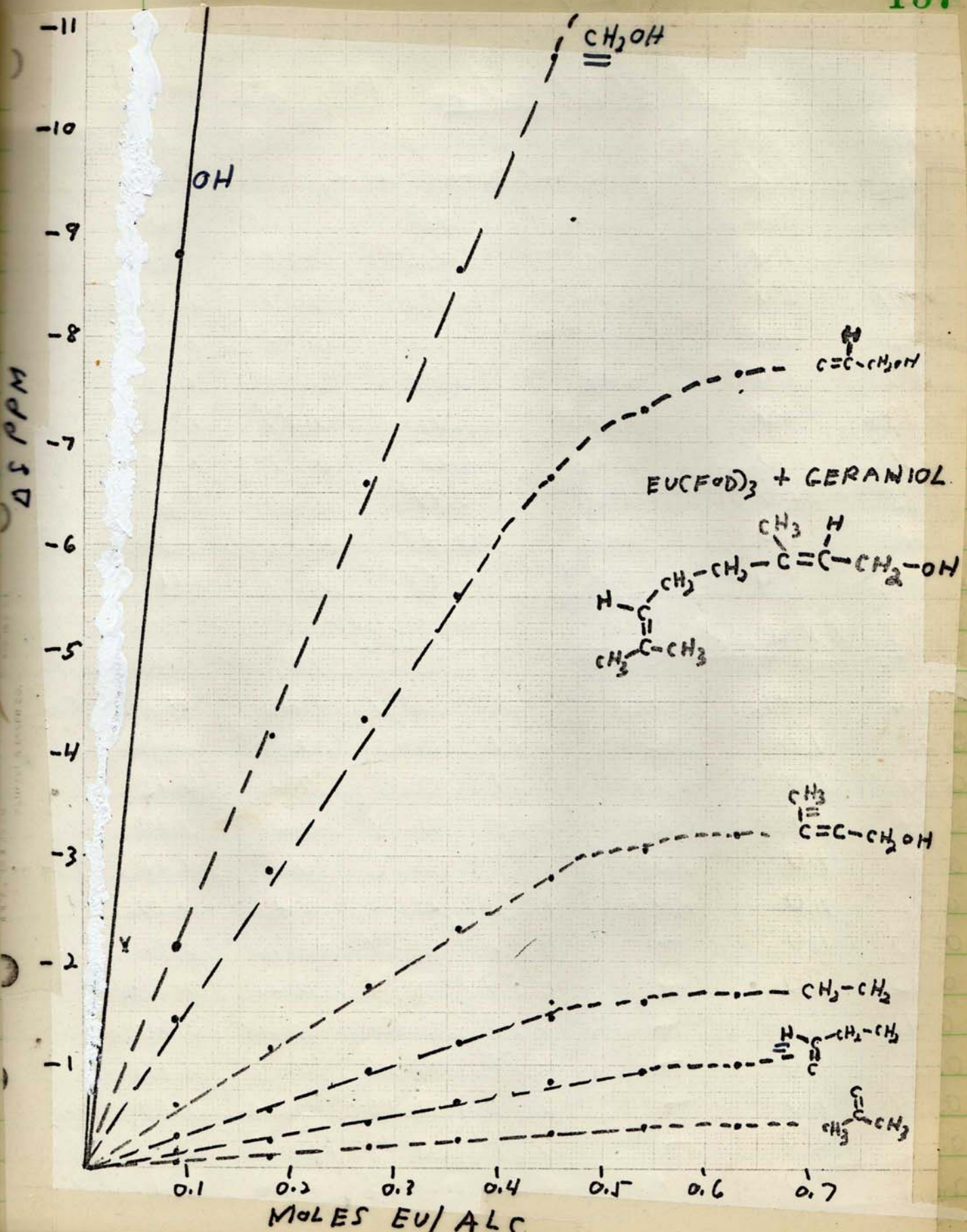
H← C=C–CH$_2$–CH$_2$ * = Rel. Internal CH$_2$Br$_2$

Eu/alc	H2 observ.*	H2 corr*	ΔH2	ΔPPM	ΔδPPM
0.00	−15	−15	0	0	0
0.09	−23	"	−8	−0.13	−0.13
0.18	−30	"	−15	−0.25	−0.12
0.27	−41	"	−26	−0.44	−0.19
0.36	−54	"	−39	−0.65	−0.21
0.45	−66	"	−51	−0.85	−0.20
0.54	−71	"	−56	−0.94	−0.09
0.63	−73	"	−58	−0.97	−0.03
		Terminal methyl			
0.00	+196	+196	0	0	0
0.09	+194	"	−2	−0.03	−0.03
0.18	+189	"	−7	−0.12	−0.09
0.27	+183	"	−13	−0.20	−0.08
0.36	+180	"	−16	−0.27	−0.07
0.45	+176	"	−20	−0.33	−0.06
0.54	+173	"	−23	−0.38	−0.05
0.63	+172	"	−24	−0.40	−0.02

Conclusions from Eu(FOD)$_3$ + Geraniol studies

(CH$_3$)(CH$_3$)>C=C(H2)–CH$_2$–CH$_2$–C(CH$_3$)=C(H$_1$)–CH$_2$OH

a) H$_1$ separates to clean triplet 7 ≅ 6 Hz
b) +6 CH$_2$–CH$_2$ protons do not separate even at Eu/alc 0.6
c) H$_2$ is separated but is very broad.
d) the terminal CH$_3$ groups partially separate at ca 0.4 Eu/alc.



ΔS PPM
0
-0.13
-0.12
-0.19
-0.21
-0.20
-0.09
-0.03

0
-0.03
-0.09
-0.08
-0.07
-0.06
-0.05
-0.02

6

Eu/alc

$Eu(FOD)_3$ Studies

[redacted] Standard Proton = 1.0

Induced Shift Ratios

Ratio = Observed Shift / Shift of 1 proton in molecule

* = not an average

6/14/73

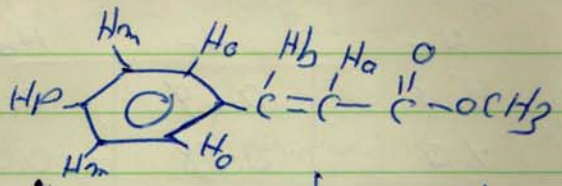
Methyl Sorbate $CH_3-\overset{H\Delta}{C}=\overset{H\gamma}{C}-\overset{H\beta}{C}=\overset{H\alpha}{C}-\overset{O}{\overset{\|}{C}}-OCH_3$

Eu/Ester	Hα	OCH_3	Hβ	Hγ	HΔ	CH_3
0.03	1.0	1.06	0.62*	0.19	0.19*	0.06
0.07	1.0	1.02	0.99	0.17	0.14	0.05
0.12	1.0	1.05	1.00	0.14*	0.14	0.03
0.17	1.0	[redacted] 1.07	0.99	0.19	0.13	0.04
0.23	1.0	1.05	1.01	0.27	0.16	0.04
0.30	1.0	1.06	1.00	0.25	0.09	0.04
0.35	1.0	1.06	0.99	0.25	0.08	0.04
0.40	1.0	1.06	0.95	0.24	0.07	0.04
Average	1.0	1.05	0.99	0.22	0.11	0.04

Salsolaldehyde $CH_3-\overset{He}{C}=\overset{Hd}{C}-\overset{Hc}{C}=\overset{Hb}{C}-CH_3OHa$

Eu/ald.	Hb	Ha	Hc	Hd	He	HF	CH_3
0.05	1.0	3.82	0.49	0.49	0.33*	0.26*	0.06
0.09	1.0	4.00	0.59	0.59	0.26	0.15	0.06
0.14	1.0	3.95	0.64	0.53	0.25	0.10	0.05
0.18	1.0	4.05	0.58	0.56	0.25	0.11	0.05
0.23	1.0	4.00	0.57	0.54	0.23	0.10	0.04
0.27	1.0	—	0.57	0.54	0.22	0.10	0.04
0.32	1.0	—	0.57	0.54	0.21	0.11	0.04
0.41	1.0	—	0.55	0.52	0.20	0.09	0.04
0.52	1.0	—	0.55	0.50	0.19	0.10	0.04
0.64	1.0	—	0.55	0.48	0.19	0.10	0.04
0.83	1.0	—	0.55	0.49	0.18	0.10	0.03
Average	1.0	3.96	0.56	0.53	0.22	0.11	0.05

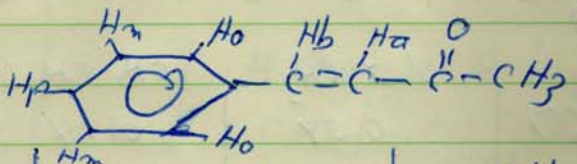
Methyl Cinnamate



* = not in average

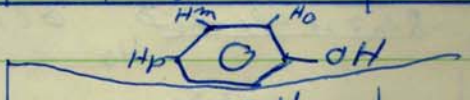
# CH_3	Eu/Este	Ha	OCH_3	Hb	Ho	Hm+p
0.06	0.09	1.0	0.98	0.99	0.22	0.05
0.05	0.18	1.0	0.99	0.98	0.21	0.04
0.03	0.27	1.0	0.96	0.98	0.18	0.03
0.04	0.36	1.0	1.00	0.97	0.17	0.03
0.04	0.53	1.0	1.01	0.96	0.15	0.03
0.04	Average	1.0	0.99	0.96	0.19	0.04
0.04						
0.04						
0.04						

4-Phenyl-3-Buten-2-one



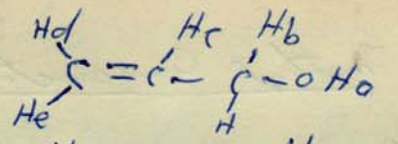
	Eu/Ketone	Ha	CH_3	Hb	Ho	Hm+p
CH_3	0.09	1.0	1.05	0.82	0.27*	0.05
.06	0.18	1.0	1.06	0.84	0.24	0.05
.06	0.27	1.0	1.04	0.82	0.21	0.06
.05	0.37	1.0	1.04	0.80	0.20	0.06
.05	0.55	1.0	1.06	0.82	0.19	0.06
.04	0.73	1.0	1.08	0.84	0.19	0.06
.04	AVE.	1.0	1.05	0.82	0.21	0.06
.04						

Phenol



Eu/alc.	Ha	OH	Hm	Hp
0.06	1.0	7.40	0.74*	0.28
0.11	1.0	6.47	0.48	0.27
0.22	1.0	6.16	0.36	0.25
0.33	1.0	—	0.33	0.24
0.44	1.0	—	0.31	0.24
0.55	1.0	—	0.31	0.23
Average	1.0	6.63	0.36	0.25

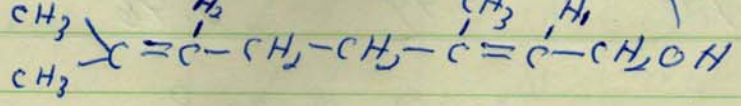
allyl alcohol



* = not in average

Eq/alc.	Hb	Ha	Hc	Hd	He
0.05	1.0	4.3	0.64	0.15*	0.75*
0.10	1.0	4.0	0.58	0.25	0.66
0.15	1.0	4.0	0.58	0.27	0.62
0.20	1.0	—	0.57	0.28	0.60
0.25	1.0	—	0.57	0.28	0.59
0.30	1.0	—	0.55	0.28	0.56
0.39	1.0	—	0.63	0.32	0.65
average	1.0	4.1	0.59	0.28	0.61

Geraniol



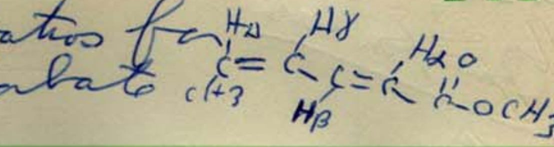
Eq/alc.	CH_2	H_1	Int. CH_3	CH_2-CH_2	H_2	Terminal CH_3
0.09	1.0	0.67	0.29	0.14	0.06	0.02
0.18	1.0	0.68	0.27	0.14	0.06	0.03
0.27	1.0	0.66	0.27	0.14	0.07	0.03
0.36	1.0	0.65	0.27	0.14	0.08	0.03
0.45	1.0	0.63	0.26	0.14	0.08	0.03
0.54	1.0	0.61	0.26	0.13	0.08	0.03
0.63	1.0	0.61	0.25	0.13	0.08	0.03
AVE.	1.0	0.64	0.27	0.14	0.07	0.03

Benzyl alcohol ϕCH_2OH

Eq/alc.	CH_2	OH	Ho	Hm+p
0.08	1.0	4.00	0.50	0.15
0.17	1.0	3.84	0.50	0.15
0.25	1.0	++	0.51	0.15
0.34	1.0	—	0.50	0.14
0.51	1.0	—	0.49	0.13
0.69	1.0	—	0.47	0.13
0.88	1.0	—	0.46	0.13
average	1.0	3.92	0.49	0.14

te
75 *
66
62
60
59
56
65
61

terminal CH_3
0.02
0.03
0.03
0.03
0.03
0.03
0.03
0.03

Induced Shift Ratios for $\Delta\gamma$ cis methyl Sorbate 

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Ratio A = $\dfrac{\delta \text{ group in } \gamma\Delta \text{ \underline{cis}}}{\delta \text{ same group in all \underline{trans}}}$

Eu/Ester	Hα	Hβ	OCH_3	Hγ	HΔ	CH_3
0.35	0.93	0.97	0.89	0.98	≅1	1.18

Ratio B = $\dfrac{\Delta\delta \text{ group in } \gamma\Delta \text{ \underline{cis}}}{\Delta\delta \text{ H}\alpha \text{ in } \gamma\Delta \text{ \underline{cis}}}$

Eu/Ester	Hα	HB	OCH_3	Hγ	HΔ	CH_3
0.35	1.0	1.08	1.01	0.18	0.07	0.146

The numbers indicate:

a) all protons except HΔ and the terminal CH_3 groups in the γΔ cis ester shift at a slower absolute rate compared to the all trans. HΔ is about the same. The terminal CH_3 is <u>faster</u>.

b) The Hβ and terminal CH_3 groups in the γΔ <u>cis</u> ester shift at a faster relative rate (relative to Hα Δγ <u>cis</u>) than the corresponding protons in the all <u>trans</u> ester relative to Hα (all trans). The OCH_3 and Hγ are relatively slower than in the all <u>trans</u> (Compare all <u>trans</u> induced shift ratios).