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).

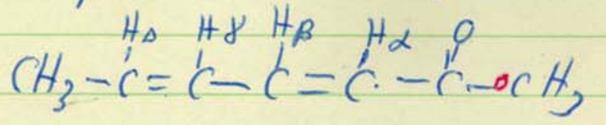
This research was performed at Temple University in 1973, sponsored under Grant No. CA-13120-02 from the National Cancer Institute.

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 ~~[illegible]~~ 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 30mg. 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 [illegible] separated!! [illegible]


$$\overset{H_\Delta}{\underset{|}{}}\quad CH_3-\overset{H_\Delta}{C}=\overset{H_\gamma}{C}-\overset{H_\beta}{C}=\overset{H_\alpha}{C}-\overset{O}{\overset{\|}{C}}-OCH_3$$

$J\alpha\beta = 16$ cps $= J\beta$ [illegible] α
$J\beta\gamma = 10$ 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.

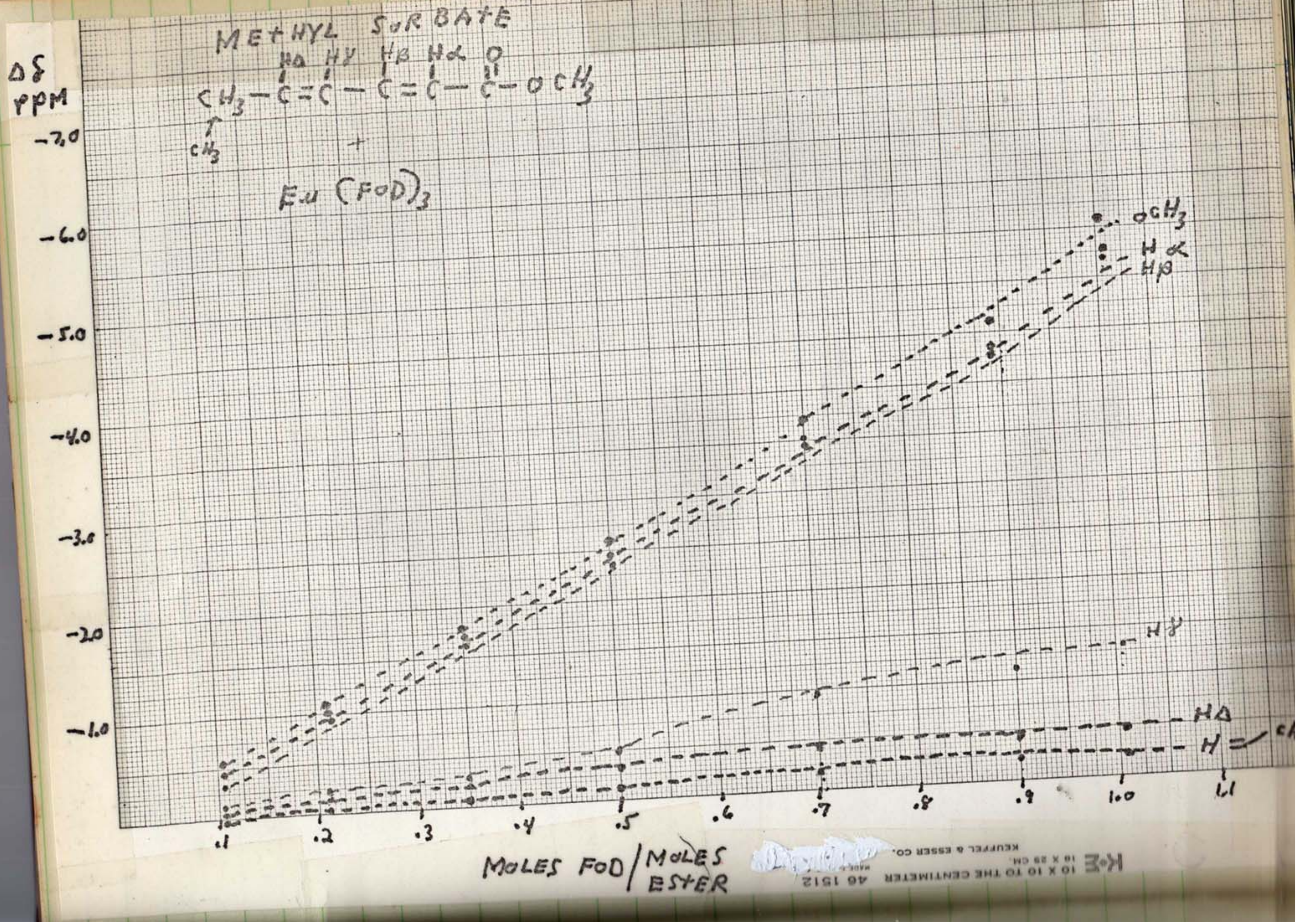
a) assuming 3 ligands per mole complex
* relative to internal CH_2Cl_2

1

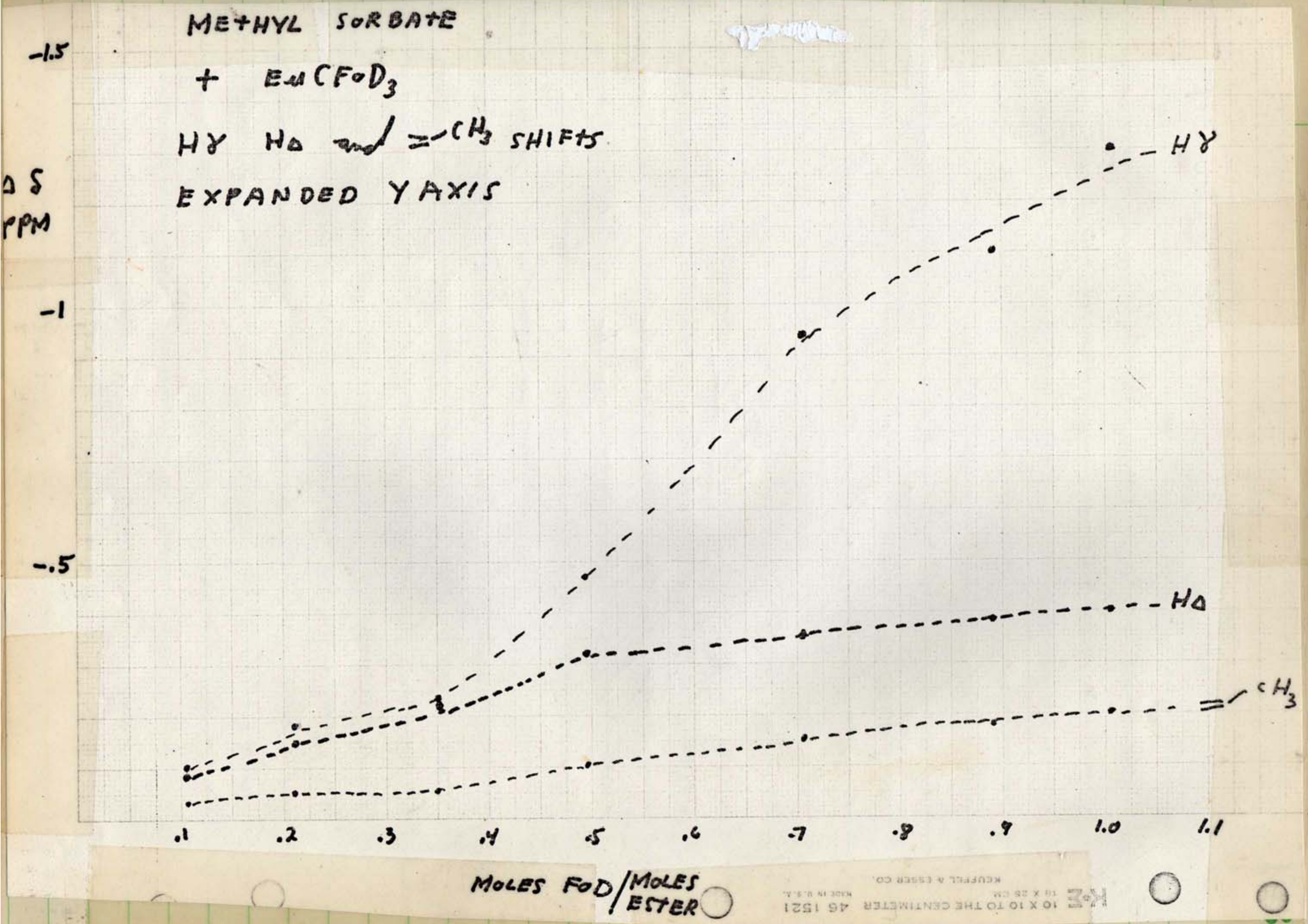
FOD/ESTER [a]	HZ Obsv.*	HZ ORIG.*	ΔHZ	Δδ PPM	Δ(Δδ PPM)
		OCH₃			
0.00	+100	+100	0	0	0
0.10	+66	"	−34	−.6	—
0.21	+35	"	−65	−1.1	−.5
0.35	−8	"	−108	−1.8	−.7
0.50	−57	"	−157	−2.6	−.8
0.70	−117	"	−217	−3.7	−1.1
0.89	−177	"	−277	−4.6	−.9
1.06	−239	"	−339	−5.6	−1.0
		Hα			
0.00	−23	−23	0	0	0
0.10	−55	"	−32	−.54	—
0.21	−87	"	−64	−1.07	−.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
		Hβ			
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 internal CH_2Cl_2

FOD/ESTER	Hz Obsv.*	Hz ORIG*	ΔHZ	ΔδPPM	Δ(ΔδPPM)
		Hγ			
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
.1
.2
.3
.4
.5
.6
.7
.8
.9
1.0
1.1
OCH3
H α
H β
H γ
H Δ
H =/ c
MOLES FOD/MOLES ESTER

MOLES FOD / MOLES ESTER

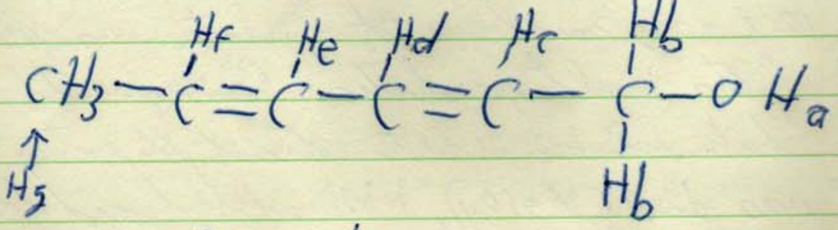


5/2/73 I.R. and n.m.r. spectra taken on commercial (Aldrich)
n.m.r. #68 sorbyl alcohol. material believed pure enough to
I.R. #180 undertake shift reagent study.

n.m.r. #69 routine sorbyl alcohol spectrum, CH_3I standard

69a	100Mg alcohol,	50mg $Eu(FOD)_3$		
69b	..	100 ..	..	
69c	..	150 ..	..	
69d	..	200 ..	..	
69e	..	250 ..	..	
69f	..	300 ..	..	
69g	..	350 ..	..	
69h	..	450 ..	..	
69i	..	550 ..	..	now all protons 1st orde
5/3/73 69j	..	700 ..	..	Completely separated, 1st ord
69k	..	.. ..	..	Protons Blown up

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



$$\overset{\uparrow}{\underset{H_g}{CH_3}}-\overset{H_f}{C}=\overset{H_e}{C}-\overset{H_d}{C}=\overset{H_c}{C}-\underset{H_b}{\overset{H_b}{C}}-OH_a$$

$J_{ab} = J_{ba} = 0$

$J_{bc} = J_{cb} = 5 HZ$

$J_{cd} = J_{dc} = 14 HZ$

$J_{de} = J_{ed} = 9 HZ$

$J_{ef} = J_{fe} = 14 HZ$

$J_{fg} = J_{gf} = 5.5 HZ$

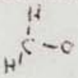
the data was put in Tabular and graphical form (se

Eu(FOD)$_3$ Experiment
SORBOYL ALCOHOL

Hz

OH

* = Rel to internal CH$_3$I

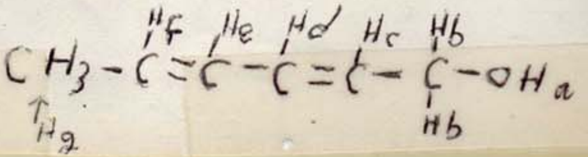
Eu / ALC	Hz obsv.*	Hz orig.	Δ Hz	Δ δ PPM	Δ (Δ δ PPM)
0.00	−97	−97	0	0	0
0.046	−359	−97	−262	−4.37	0
0.0915	−594	−97	−497	−8.30	−3.93
0.137	−840	−97	−743	−12.35	−4.05
0.183	−1103	−97	−1006	−16.67	−4.32
0.229	−1360	−97	−1263	−21.00	−4.33
			Hb		
0.00	−109	−109	0	0	0
0.046	−175	−109	−66	−1.1	0.00
0.0915	−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	−442	−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 **Hc**	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

Hd

Eu/Alcohol	H2 Obser.	H2 orig.	ΔH_2	$\Delta\delta$ PPM	$\Delta(\Delta\delta$ 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	−5.26	−1.10
0.515	−557	−213	−344	−5.74	−0.54
0.640	−575	−213	−362	−6.03	−0.29

He

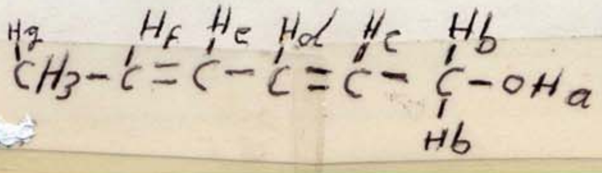
Eu/Alcohol	H2 Obser.	H2 orig.	ΔH_2	$\Delta\delta$ PPM	$\Delta(\Delta\delta$ PPM).
0.00	−213	−213	0	0	0
0.046	−235	−213	−22	−0.37	0
0.0915	−245	−213	−32	−0.54	−0.17
0.137	−260	−213	−47	−0.79	−0.25
0.183	−275	−213	−62	−1.03	−0.24
0.229	−285	−213	−72	−1.20	−0.17
0.274	−297	−213	−84	−1.40	−0.20
0.320	−310	−213	−97	−1.62	−0.22
0.412	−330	−213	−117	−1.95	−0.33
0.515	−340	−213	−127	−2.12	−0.17
0.640	−353	−213	−140	−2.34	−0.22

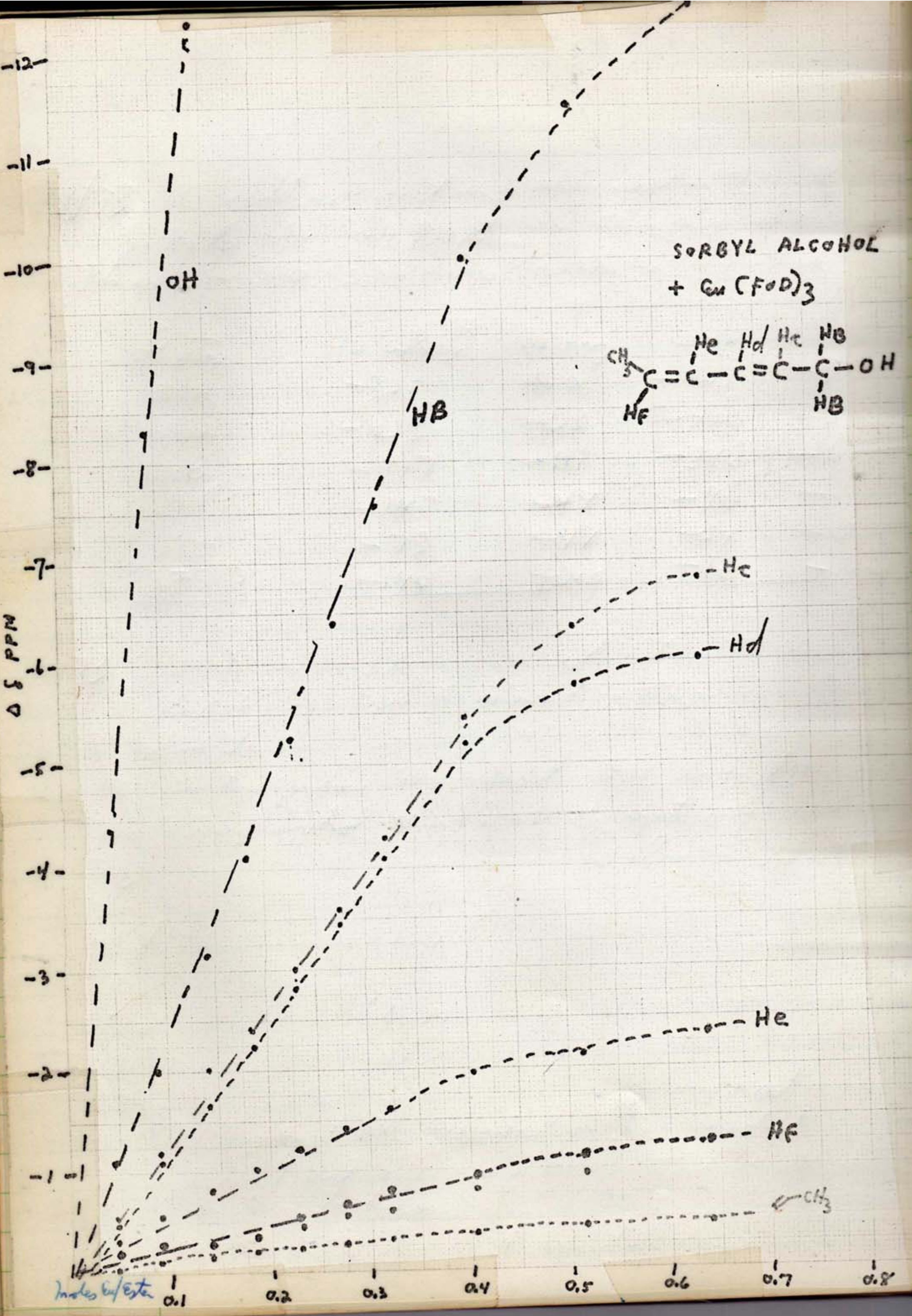


$$\underset{\uparrow H_g}{CH_3}-\overset{H_f}{C}=\overset{H_e}{C}-\overset{H_d}{C}=\overset{H_c}{C}-\underset{H_b}{\overset{H_b}{C}}-OH_a$$

H_F

Eu / Alcohol	Hz Observ.	Hz ORIG.	Δ Hz	Δ δ PPM	Δ CΔ δ PPM
0.00	−213	−213	0	0	0
0.046	−230.5	−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_g		
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

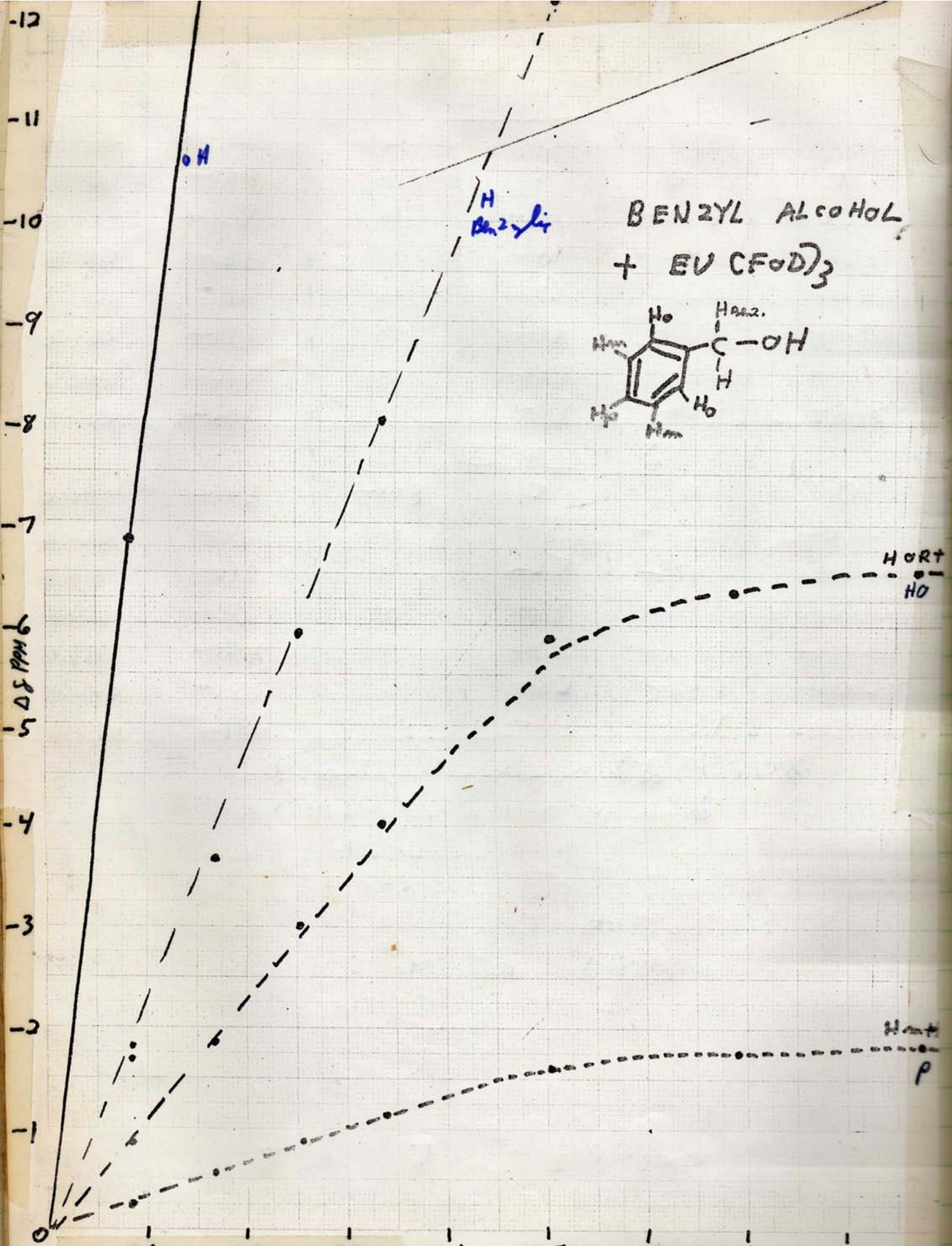

$\overset{H_g}{CH_3}-\overset{H_f}{C}=\overset{H_e}{C}-\overset{H_d}{C}=\overset{H_c}{C}-\underset{H_b}{\overset{H_b}{C}}-OH_a$


SORBYL ALCOHOL
+ Eu (FOD)3
CH3
He
Hd
Hc
HB
C=C—C=C—C—OH
HF
HB
OH
HB
Hc
Hd
He
HF
CH3
Δ δ 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

Eu/alc.	Hz observ.*	Hz orig.*	Δ Hz	Δ δ PPM.	Δ(Δδ PPM)
		OH			
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)$_3$
H$_o$
H$_{benz.}$
C—OH
H
H$_m$
H$_o$
H$_p$
H$_m$
OH
H Benzylic
H ORT
HO
H m+
P
-12
-11
-10
-9
-8
-7
-6
-5
-4
-3
-2
-1
0
Δ δ PPM
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
MOLES EU / MOLES ALCOHOL

5/1

5/16

5/17

φ

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 $Eu(FOD)_3$. H ortho 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.	Hz observ.*	Hz orig.*	ΔHz	Δδ PPM	Δ(ΔδPPM)
		OH			
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
		H ORTHO			
0.000	−118	−118	0	0	0
0.055	−164	−118	−46	−0.77	−0.77
0.110	−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)$_3$

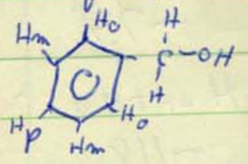
H META

Eu/alc.	Hz Observ.	Hz orig.	ΔHz	Δδ PPM	Δ(Δδ 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

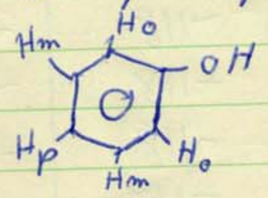
H PARA

Eu/alc.	Hz Observ.	Hz orig.	ΔHz	Δδ PPM	Δ(Δδ PPM)
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

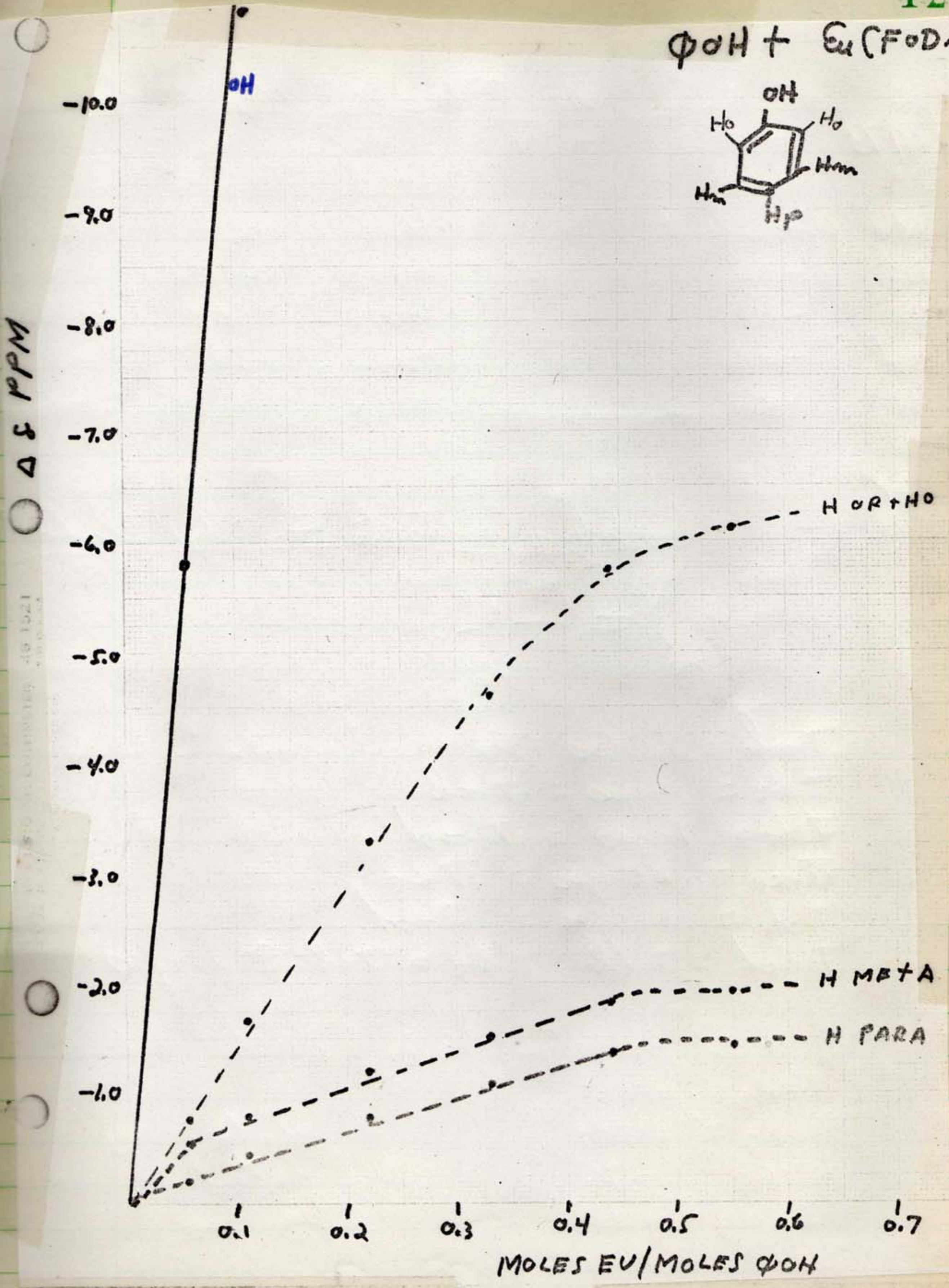


J om = J mo = 7.0 cps
J op = J po = 2.5 cps
J mp = J pm = 7 cps.



J om = J mo = 8.0 cps
J op = J po = 1.5 cps
J mp = J pm = 7.5 cps

φOH + Eu(FOD)$_3$

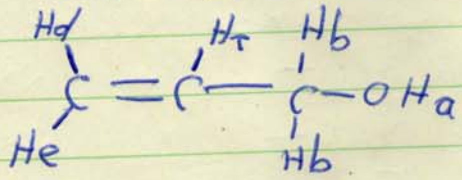

OH
Ho
Ho
Hm
Hm
Hp
OH
-10.0
-9.0
-8.0
-7.0
-6.0
-5.0
-4.0
-3.0
-2.0
-1.0
Δδ PPM
H ORTHO
H META
H PARA
0.1
0.2
0.3
0.4
0.5
0.6
0.7
MOLES EU/MOLES φOH

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$_3$I standard
73b 55 Mg allyl alcohol + 50 Mg Eu(FOD)$_3$
73c " " " " + 100 " "
73d " " " " 150 " "
73e " " " " 200 " " Spectrum much broader
73f " " " " 250 " " "
73g " " " " 300 " " "

Coupling Constants for allyl alcohol

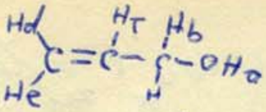


J ab = 5.5 cps = J ba (seen only in conc. solution, decouples with Eu).
J bc = 5 cps = J cb
J dc = 11 cps = J cd
J ce = 17.5 cps = J ec
J de = 1.5 cps = J ed
J bd = J db = J be = J eb ≅ 1 cps

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.

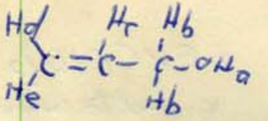


$(H_d)(H_e)C{=}C(H_T){-}C(H_b)(H){-}OH_a$

ALLYL ALCOHOL + EU(FOD)$_3$

* rel. to internal CH_3I

EU/ALC.	HZ OBS.*	HZ ORIG.*	ΔHZ	Δ PPM	Δ(Δδ PPM
			OH		
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
			Hb		
0.000	−124	−124	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
			HT		
0.000	−229	−229	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



$H_d H_e C=C(H_c)-C(H_b)(H_b)-OH_a$

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

* rel. internal CH_3I

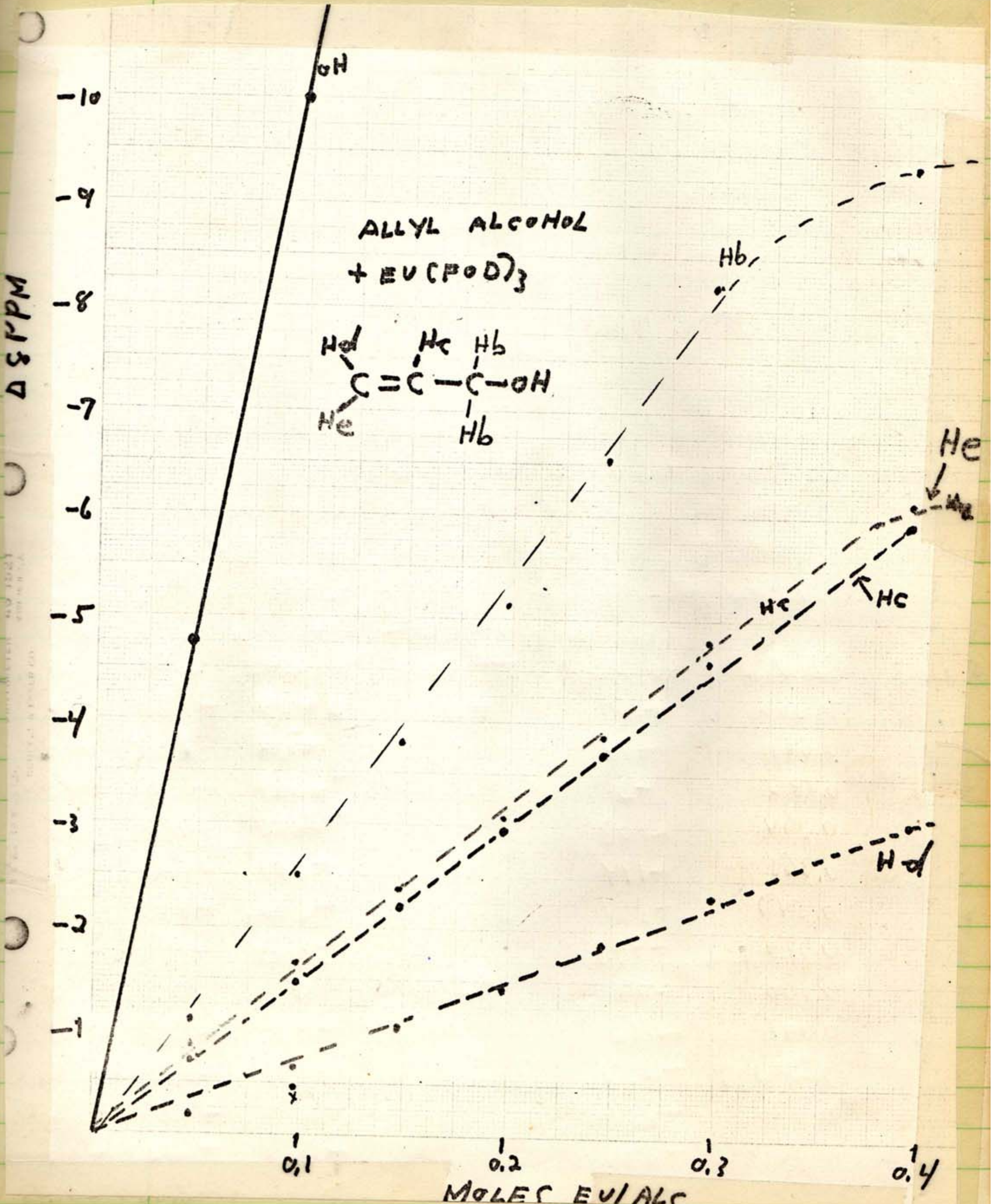
Eu/alc.	H2 observ.*	H2 orig.* He	ΔH2	ΔPPM	Δ(ΔδPPM)
0.000	−174	−174	0	0	0
0.049	−224	"	−50	−0.84	−0.84
0.098	−273	"	−99	−1.65	−0.81
0.148	−316	"	−142	−2.37	−0.72
0.197	−359	"	−185	−3.08	−0.71
0.246	−406	"	−232	−3.87	−0.79
0.295	−461	"	−287	−4.79	−0.92

5/21/73 An additional point was taken. 55 Mg allyl alcohol + 400 Mg Eu FOD

N.M.R. #73L Eu/alc = 0.392

Proton	H2 observ.	H2 Orig.	ΔH2.	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)$_3$
Hd
Hc
Hb
C=C—C—OH
He
Hb
OH
Hb
He
Hc
He
Hd
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$_2$Cl$_2$. Routine Spectrum

74a ″ ″ ″ + 50 Mg Eu(FOD)$_3$.

74b ″ ″ ″ +100 Mg ″

74c ″ ″ ″ 150 Mg ″

74d ″ ″ ″ 200 Mg ″

74e ″ ″ ″ +300 Mg ″

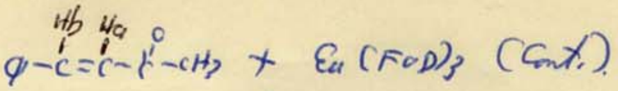
74f ″ ″ ″ + 400 Mg ″

during the addition H$_a$ gradually overtook H$_b$ resulting in an 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$_2$Cl$_2$

5/23/73

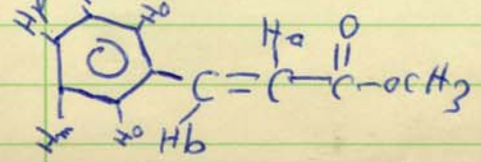
Eu/ketone	Hz obsv*	$\underline{CH_3}$ Hz orig*	ΔHz	ΔPPM	Δ(δPPM)
0.000	+181	+181	0	0	0
0.091	+94	″	-87	-1.45	-1.45
0.182	-2	″	-183	-3.05	-1.60
0.274	-103	″	-284	-4.74	-1.69
0.365	-199	″	-380	-6.35	-1.61
0.547	-361	″	-542	-9.03	-2.68
0.730	-443	″	-624	-10.40	-1.37
0.000	-79	$\underline{H_a}$ -79	0	0	0
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


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

* rel. internal CH_2Cl_2

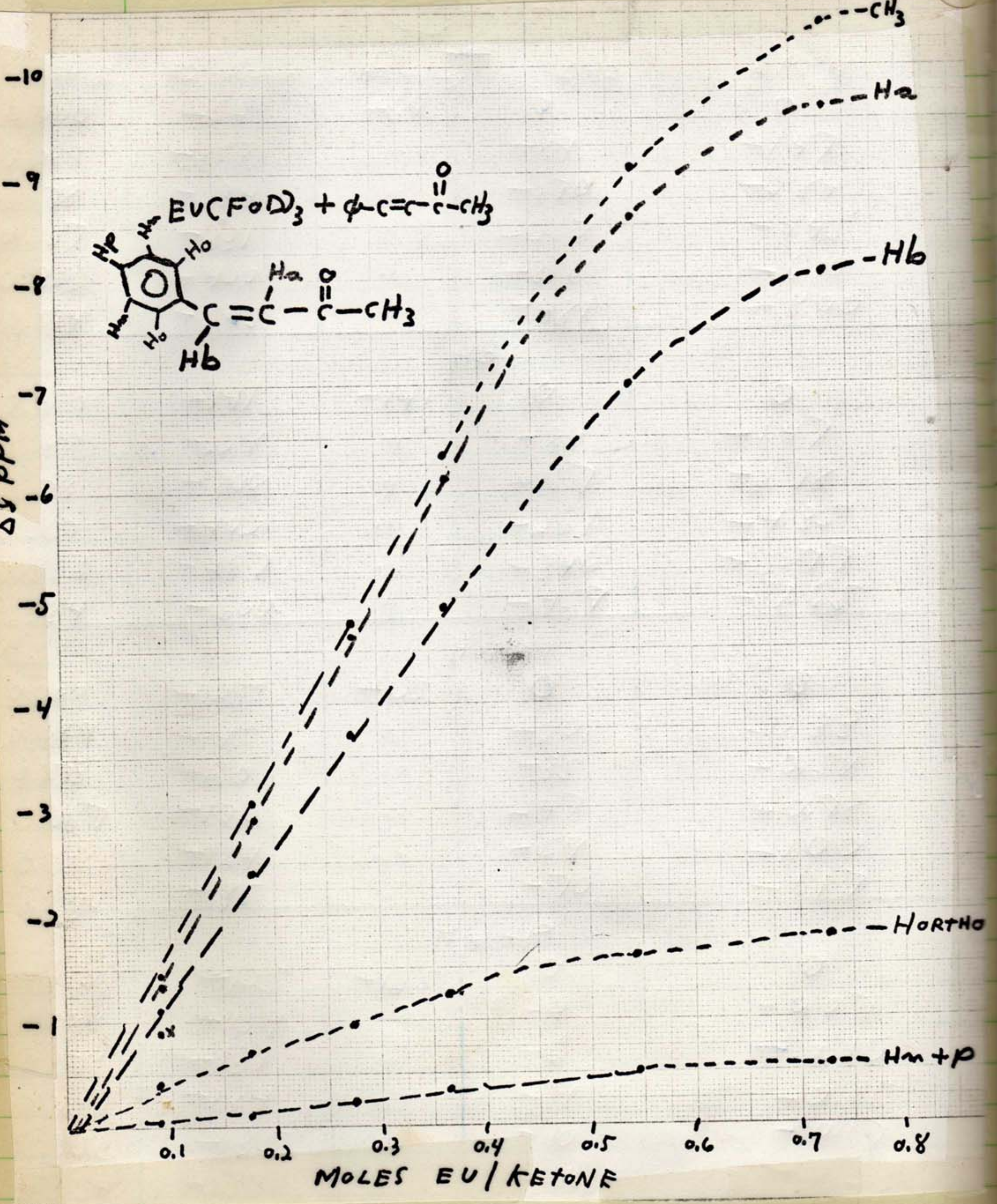
EU/Ketone	Hz observ*	Hz orig.*	ΔHz	ΔPPM	Δ(δPPM)
		Hb			
0.000	−129	−129	0	0	0
0.091	−197	"	−68	−1.13	−1.13
0.182	−274	"	−145	−2.42	−1.29
0.274	−353	"	−224	−3.74	−1.32
0.365	−422	"	−293	−4.89	−1.15
0.547	−549	"	−420	−7.00	−2.11
0.730	−612	"	−483	−8.05	−1.05
		Hortho			
0.000	−124	−124	0	0	0
0.091	−146	"	−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

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

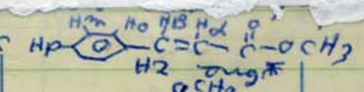


Jab = Jba = 16 cps
Jom = Jmo = 7.5 cps
Jop = Jpo = 2.0 cps
Jmp = Jpm = 7.5 cps

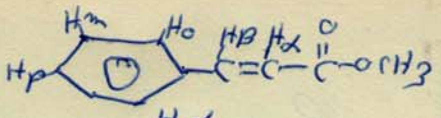
CH_2Cl_2
Δ(δPPM)
0
1.45
1.60
.69
.61
.68
1.37
0
1.38
50
.69
.55
.43
.06


Eu(FOD)3 + φ-C=C-C(=O)-CH3
Hp
Hm
Ho
Hm
Ho
Ha
C=C-C(=O)-CH3
Hb
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

* = rel. internal CH_2Cl_2

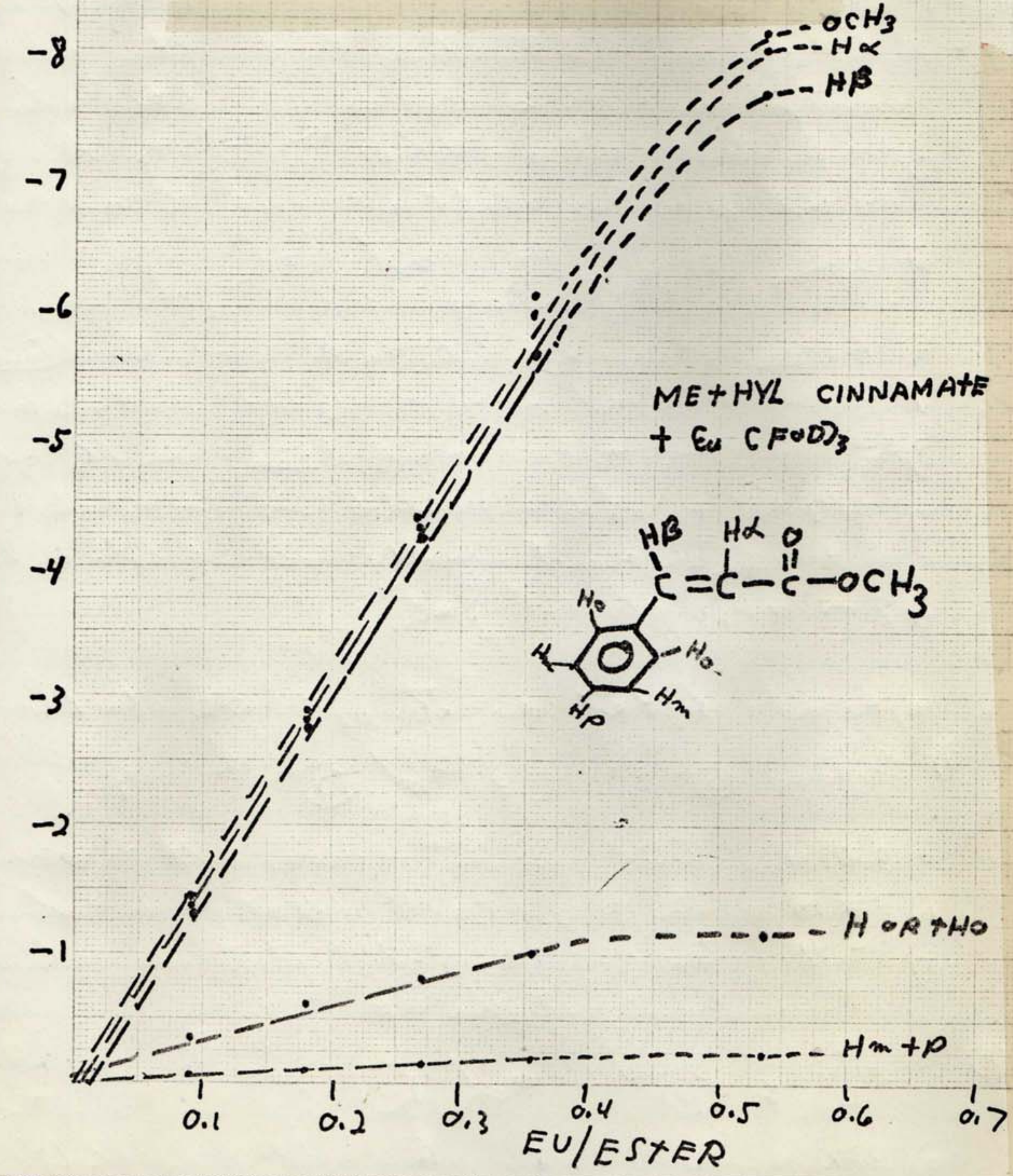
Eu/Ester	Hz observ.*	 Hz orig.*	ΔHz	− ΔPPM
0.000	+92	+92	0	0
0.089	+5	"	−87	−1.45
0.178	−77	"	−169	−2.82
0.267	−173	"	−265	−4.42
0.356	−264	"	−356	−5.95
0.534	−397	"	−489	−8.16

130



Hα

Eu/[illegible] ester	Hz observ.	Hz orig.	ΔHz	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
			H ORTHO	
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



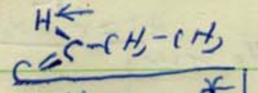
Δ δ PPM
-8
-7
-6
-5
-4
-3
-2
-1
0.1
0.2
0.3
0.4
0.5
0.6
0.7
EU/ESTER
OCH$_3$
Hα
Hβ
H oR + Ho
Hm + P
METHYL CINNAMATE
+ Eu (FOD)$_3$
Hβ
Hα
O
C=C—C—OCH$_3$
Ho
Ho
Hm
Hp

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

$\overset{H}{*C} = C-CH_2OH$

Eu/alc.	Hz obsv*	Hz orig.	Δ Hz	Δ PPM	Δ δPPM
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

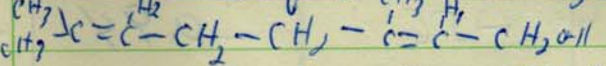
Eu(FOD)$_3$ + Geraniol (Contd)


$H\leftarrow C(=C)-CH_2-CH_2$

* = rel. Internal CH_2Br_2

Eu/alc	H2 observ.*	H2 orig*	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


$(CH_3)_2C=\overset{H_2}{C}-CH_2-CH_2-\overset{CH_3}{C}=\overset{H_1}{C}-CH_2OH$

a) H_1 separates to clean triplet $J \cong 6Hz$

b) the 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

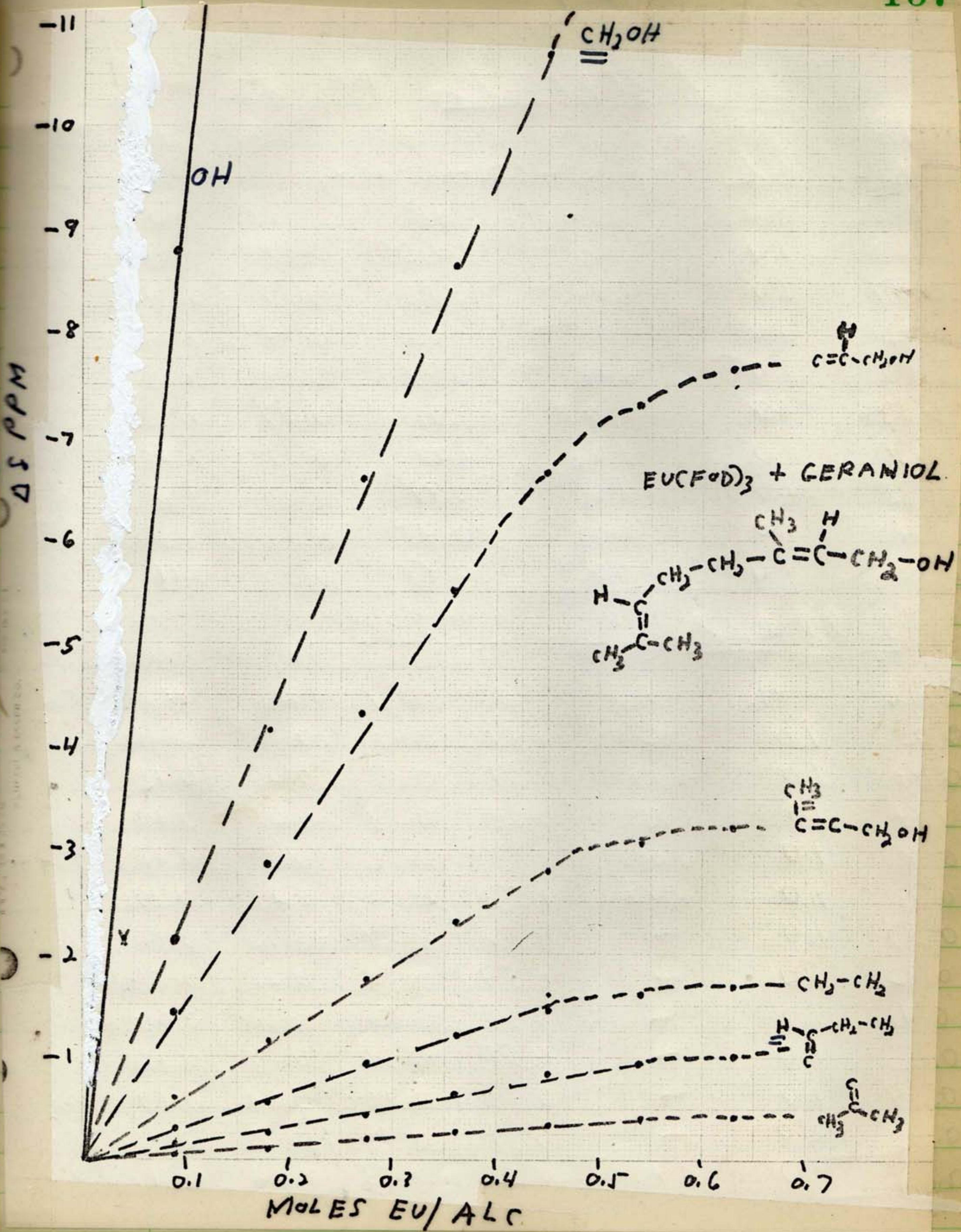
ΔδPP

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/al.



Eu(FOD)₃ Studies

Standard Proton = 1.0

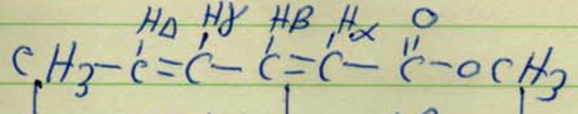
Induced Shift Ratios

Ratio = $\frac{\text{Observed Shift}}{\text{Shift of 1 proton in molecule}}$

* = not an average

6/14/73

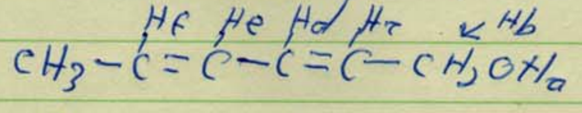
Methyl Sorbate



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

Eu/Ester	H α	OCH₃	Hβ	Hγ	HΔ	CH₃
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	1.07	0.99	0.19	0.13	0.04
0.23	1.0	1.05	1.01	0.27	0.10	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

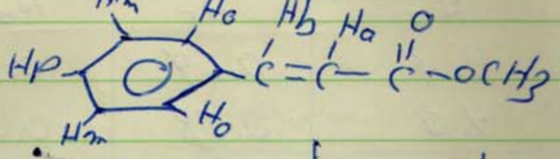
Sorbyl alcohol



$CH_3-\overset{H_f}{C}=\overset{H_e}{C}-\overset{H_d}{C}=\overset{H_c}{C}-\overset{H_b}{CH_2}OH_a$

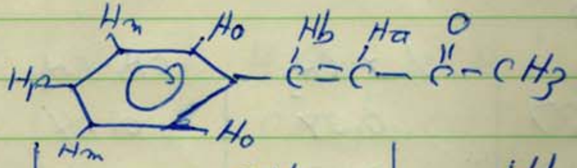
Eu/alc.	Hb	Ha	Hc	Hd	He	Hf	CH₃
0.05	1.0	3.82	0.49	0.49	0.33*	0.26*	0.06
0.09	1.0	4.00	0.59	0.59	0.26	0.15	0.06
0.14	1.0	3.95	0.64	0.53	0.25	0.10	0.05
0.18	1.0	4.05	0.58	0.56	0.25	0.11	0.05
0.23	1.0	4.00	0.57	0.54	0.23	0.10	0.04
0.27	1.0	—	0.57	0.54	0.22	0.10	0.04
0.32	1.0	—	0.57	0.54	0.21	0.11	0.04
0.41	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



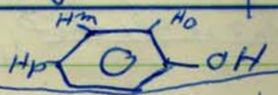
* = not in average

Eu/Ester	Ha	OCH3	Hb	Ho	Hm+p
0.09	1.0	0.98	0.99	0.22	0.05
0.18	1.0	0.99	0.98	0.21	0.04
0.27	1.0	0.96	0.98	0.18	0.03
0.36	1.0	1.00	0.97	0.17	0.03
0.53	1.0	1.01	0.96	0.15	0.03
average	1.0	0.99	0.96	0.19	0.04



4-Phenyl-3-Buten-2-One

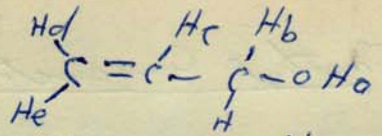
Eu/Ketone	Ha	CH3	Hb	Ho	Hm+p
0.09	1.0	1.05	0.82	0.27*	0.05
0.18	1.0	1.06	0.84	0.24	0.05
0.27	1.0	1.04	0.82	0.21	0.06
0.37	1.0	1.04	0.80	0.20	0.06
0.55	1.0	1.06	0.82	0.19	0.06
0.73	1.0	1.08	0.84	0.19	0.06
AVE.	1.0	1.05	0.82	0.21	0.06



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

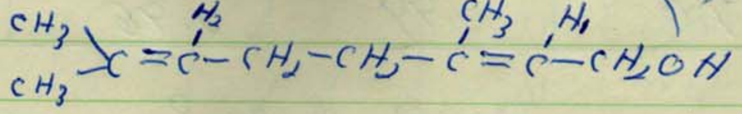
allyl alcohol


$H_dH_eC=C(H_c)-C(H_b)(H)-OH_a$

* = not in average

Eu/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

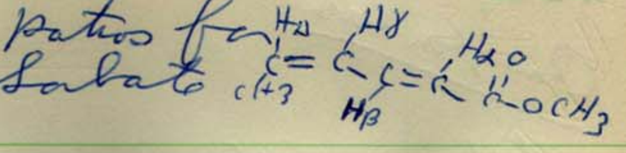

$(CH_3)_2C=C(H_2)-CH_2-CH_2-C(CH_3)=C(H_1)-CH_2OH$

Eu/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

Eu/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

Induced Shift Ratios for Δγ *cis* methyl Sorbate



6/18/73

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

Eu/Ester	Hα	Hβ	OCH3	Hγ	HΔ	CH3
0.35	0.93	0.97	0.89	0.98	≅1	1.18

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

Eu/Ester	Hα	Hβ	OCH3	Hγ	HΔ	CH3
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 CH3 groups in the γΔ cis ester shift at a slower absolute rate compared to the all trans. HΔ is about the same. The terminal CH3 is *faster*.

b) The Hβ and terminal CH3 groups in the γΔ *cis* ester shift at a faster relative rate (relative to Hα Δδ *cis*) than the corresponding protons in the all *trans* ester relative to Hα (all trans). The OCH3 and Hγ are relatively slower than in the all *trans* (Compare all *trans* induced shift ratios).

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te
75 *
66
62
60
59
56
65
61

terminal CH3
0.02
0.03
0.03
0.03
0.03
0.03
0.03
0.03

ps