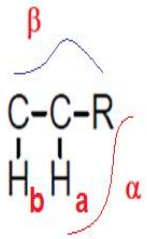
EFEITO DOS SUBSTITUINTES SOBRE O DESLOCAMENTO QUÍMICO

RMN DE H

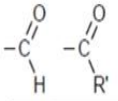
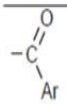
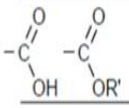


DESLOCAMENTO PADRÃO

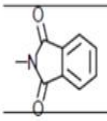
$(-CH_3)$ 0.90 δ

$(-CH_2-)$ 1.20 δ

(-CH-) 1.55 δ

Substituinte R		α	β
CLORO	$-CH_3$	2.30	0.60
	$-CH_2-$	2.30	0.55
	-CH-	2.55	0.15
BROMO	$-CH_3$	1.80	0.80
	$-CH_2-$	2.15	0.80
	-CH-	2.20	0.25
IODO	$-CH_3$	1.30	1.10
	$-CH_2-$	1.95	0.60
	-CH-	2.70	0.35
arila	$-CH_3$	1.45	0.35
	$-CH_2-$	1.45	0.55
	-CH-	1.35	----
	$-CH_3$	1.25	0.25
	$-CH_2-$	1.10	0.30
	-CH-	0.95	----
	$-CH_3$	1.70	0.28
	$-CH_2-$	1.64	0.50
	-CH-	1.76	0.76
	$-CH_3$	1.20	0.25
	$-CH_2-$	1.00	0.30
	-CH-	0.95	----

Substituinte R		α	β
$-C\equiv N$	$-CH_3$	1.10	0.45
	$-CH_2-$	1.10	0.40
	-CH-	0.95	----
-C=C-	$-CH_3$	0.90	0.05
	$-CH_2-$	0.75	0.10
	-CH-	0.65	----
$-C\equiv C-$	$-CH_3$	0.90	0.15
	$-CH_2-$	0.80	0.05
	-CH-	0.35	----
-OH	$-CH_3$	2.45	0.40
	$-CH_2-$	2.30	0.20
	-CH-	2.10	----
-O- alquila	$-CH_3$	2.45	0.30
	$-CH_2-$	2.30	0.15
	-CH-	2.10	----
-O- arila	$-CH_3$	2.95	0.40
	$-CH_2-$	2.65	0.45
	-CH-	3.06	----
	$-CH_3$	2.90	0.40
	$-CH_2-$	2.95	0.45
	-CH-	3.45	----

Substituinte R		α	β
-N(H) alquila $-N(alquila)_2$	$-CH_3$	1.25	0.20
	$-CH_2-$	1.40	0.15
	-CH-	1.35	----
-NHArila -N(alquila)(arila)	$-CH_3$	2.08	0.28
	$-CH_2-$	2.03	0.34
	-CH-	2.33	
	$-CH_3$	2.14	0.30
	$-CH_2-$	2.25	0.51
	-CH-		
$-NO_2$	$-CH_3$	3.50	0.65
	$-CH_2-$	3.15	0.85
	-CH-	3.05	----
$-N_3$	$-CH_3$	2.08	0.45
	$-CH_2-$	1.45	-0.46
	-CH-	1.46	-0.22
-SH -S- alquila	$-CH_3$	1.20	0.40
	$-CH_2-$	1.30	0.30
	-CH-	1.30	----
-S- arila	$-CH_3$	1.47	0.35
	$-CH_2-$	1.45	0.31
	-CH-	1.60	0.01

CONTINUA...

EFEITO DOS SUBSTITUINTES SOBRE O DESLOCAMENTO QUÍMICO

RMN DE H

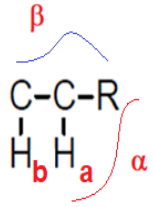
Substituinte R		α	β
$-O-SO_2Ar$	$-CH_3$	2.84	0.39
	$-CH_2-$	2.66(6)	0.28
	-CH-	3.16(3)	0.32
$-O-SO_2Me$	$-CH_3$	3.01(1)	0.47
	$-CH_2-$	2.90(5)	0.43
	-CH-	2.64(1)	0.61

Substituinte R		α	β
	$-CH_3$	1.73	0.23
	$-CH_2-$	1.54	0.63
	-CH-	1.47	
	$-CH_3$	2.13	0.37
	$-CH_2-$	1.75	0.50
	-CH-	1.53	
-Se-Ar	$-CH_3$	1.55	0.45
	$-CH_2-$	1.55	0.36
	-CH-	1.62	0.32
	CH_3	1.72	
	$-CH_2-$	1.48	
	-CH-		

Substituinte R		α	β
	$-CH_3$	2.10(1)	
	$-CH_2-$		
	-CH-		
-Te-Ph	$-CH_3$	1.20	
	$-CH_2-$	1.40	
	-CH-		
	$-CH_3$	0.58	0.22
	$-CH_2-$	0.59	0.34
	-CH-	0.44	
$-SiMe_3$	$-CH_3$	-0.90	0.06
	$-CH_2-$	-0.39	
	-CH-	-0.83	
$-SnMe_3$	$-CH_3$	-0.81	
	$-CH_2-$		
	-CH-		

ADAPTADO DE : P. L. Fuchs and C. A. Bunnell, "Carbon-13 NMR Based Spectral Problems," John Wiley, New York, 1979.

Hans J. Reich, http://www.chem.wisc.edu/areas/reich/nmr/notes-9-hmr-5-curphy-morrison.pdf)



DESLOCAMENTO PADRÃO

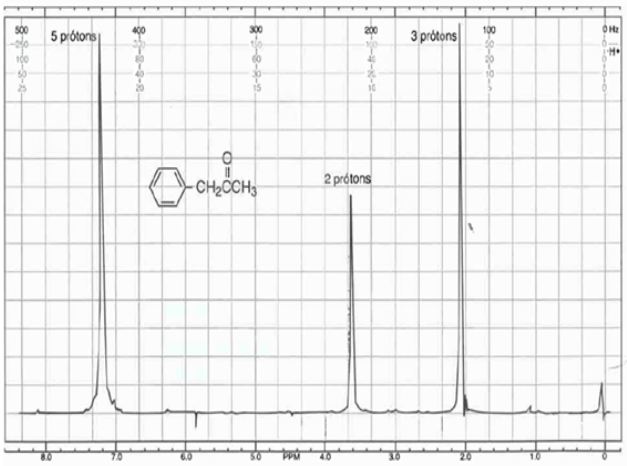
(-CH_3) 0.90 δ

(-CH_2-) 1.20 δ

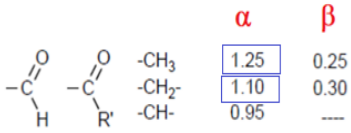
(-CH-) 1.55 δ

δ = deslocamento padrão + Σ α + Σ β

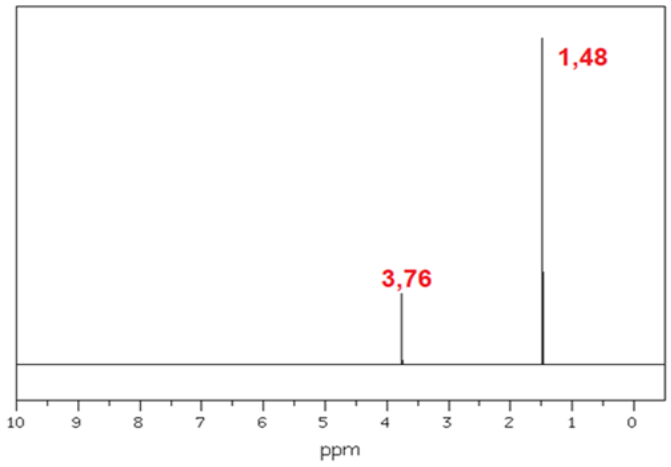
δ_{CH_3} = 0,90 + 1,25 = 2,15 ppm

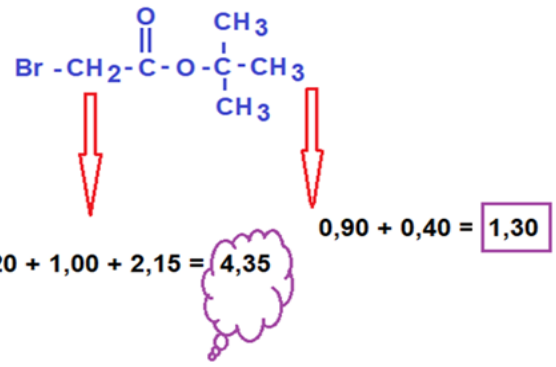


δ_{CH_2} = 1,20 + 1,10 + 1,45 = 3,75 ppm



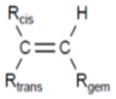
		α	β
	-CH_3	1.25	0.25
	-CH_2-	1.10	0.30
	-CH-	0.95	----
arila	-CH_3	1.45	0.35
	-CH_2-	1.45	0.55
	-CH-	1.35	----





Se os substituintes forem muito elétron-atraentes, poderá haver maior diferença entre o calculado e o experimental.

		α	β
	-CH_3	1.20	0.25
	-CH_2-	1.00	0.30
	-CH-	0.95	----
alquila	-CH_3	2.90	0.40
	-CH_2-	2.95	0.45
	-CH-	3.45	----
BROMO	-CH_3	1.80	0.80
	-CH_2-	2.15	0.80
	-CH-	2.20	0.25

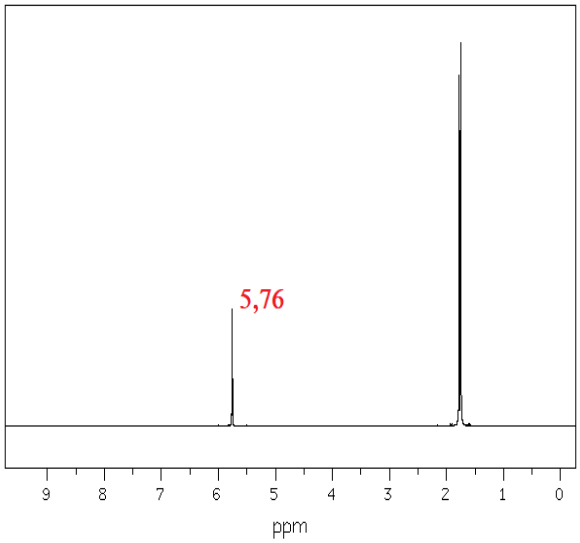


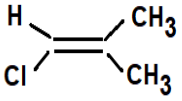
$\delta_{C=CH} = 5.25 + Z_{gem} + Z_{cis} + Z_{trans}$

Substituent R	Zi R (ppm) Zgem	Zcis	Ztrans
H	0.0	0.0	0.0
Alquila	0.45	-0.22	-0.28
Alquila cíclico	0.69	-0.25	-0.28
CH_2OH	0.64	-0.01	-0.02
CH_2SH	0.71	-0.13	-0.22
CH_2X (X = F, Cl, Br)	0.70	0.11	-0.04
CH_2NR_2	0.58	-0.10	-0.08
CF_3	0.66	0.61	0.32
$C{=}CR_2$	1.00	-0.09	-0.23
C≡C-R	0.47	0.38	0.12
C≡N	0.27	0.75	0.55
COOH	0.97	1.41	0.71
COOR	0.80	1.18	0.55
C(O)H	1.02	0.95	1.17
$C(O)NR_2$	1.37	0.98	0.46
C(O)Cl	1.11	1.46	1.01
C=O	1.10	1.12	0.87
CH_2-C(O)R; CH_2-CN	0.69	-0.08	-0.06
CH_2Ar	1.05	-0.29	-0.32
Ar	1.38	0.36	-0.07
Ar (o-subs)	1.65	0.19	0.09

Substituent R	Zi R (ppm) Zgem	Zcis	Ztrans
F	1.54	-0.40	-1.02
Cl	1.08	0.18	0.13
Br	1.07	0.45	0.55
I	1.14	0.81	0.88
OR **(R é alifático)**	1.22	-1.07	-1.21
OR **(R é substituído)**	1.21	-0.60	-1.00
O-C(O)-R	2.11	-0.35	-0.64
$O\text{-}P(O)(OEt)_2$	0.66	0.88	0.67
SR	1.11	-0.29	-0.13
S(O)R	1.27	0.67	0.41
$S(O)_2R$	1.55	1.16	0.93
S-C N	0.80	1.17	1.11
SF_5	1.68	0.61	0.49
SePh (5)	1.36	0.17	0.24
Se(O)Ph	1.86	0.97	0.63
$Se(O_2)Ph$	1.76	1.49	1.21
NR_2 **(R é alifatico)**	0.80	-1.26	-1.21
NR_2 **(R é substituído)**	1.17	-0.53	-0.99
N=N-Ph	2.39	1.11	0.67
NO_2	1.87	1.30	0.62
N-C(O)R	2.08	-0.57	-0.72
N_3	1.21	-0.35	-0.71[2]
$P(O)(OEt)_2$	0.66	0.88	0.67
$SiMe_3$	0.77	0.37	0.62
$GeMe_3$	1.28	0.35	0.67

Pascual, C. *Helv. Chem. Acta* **1966**, *49*, 164. L'Abbe, G. *Chem. & Ind. (London)* **1971**, 278





δ = 5,25 + 1,08 - 0,22 - 0,28 = 5,83 ppm

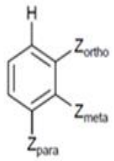
δ padrão = 7,36 ppm

Substituinte R	Zi R (ppm) Z orto	Zmeta	Zpara
H	0.0	0.0	0.0
CH_3[a]	-0.18	-0.11	-0.21
$C(CH_3)_3$	0.02	-0.08	-0.21
CH_2Cl	0.02	-0.01	-0.04
CH_2OH	-0.07	-0.07	-0.07
CF_3	0.32	0.14	0.20
CCl_3	0.64	0.13	0.10
$CH{=}CH_2$	0.04	-0.04	-0.12
CH=CHCOOH	0.19	0.04	0.05
C C-H	0.15	-0.02	-0.01
C C-Ph	0.17	-0.02	-0.03
Ph	0.23	0.07	-0.02
COOH	0.77	0.11	0.25
$C(O)OCH_3$	0.68	0.08	0.19
C(O)OPh	0.85	0.14	0.27
$C(O)NH_2$	0.46	0.09	0.17
C(O)Cl	0.76	0.16	0.33
$C(O)CH_3$	0.60	0.10	0.20
$C(O)C(CH_3)_3$	0.44	0.05	0.05
C(O)H	0.53	0.18	0.28
C(NPh)H	0.6	0.2	0.2
C(O)Ph	0.45	0.12	0.23
C(O)C(O)Ph	0.62	0.15	0.30
CN	0.29	0.12	0.25

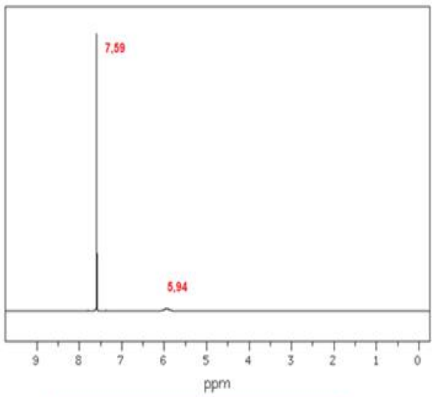
Substituinte R	Zi R (ppm) Z orto	Z meta	Zpara
OPh	-0.36	-0.04	-0.28
$O\text{-}C(O)CH_3$	-0.27	-0.02	-0.13
O-C(O)Ph	-0.14	0.07	-0.09
$O\text{-}SO_2Me$	-0.05	0.07	-0.01
SH	-0.08	-0.16	-0.22
SMe	-0.08	-0.10	-0.24
SPh	0.06	-0.09	-0.15
SO_2Cl	0.76	0.35	0.45
NH_2	-0.71	-0.22	-0.62
NMe_2	-0.66	-0.18	-0.67
NEt_2	-0.68	-0.15	-0.73
$NMe_3{+}I^-$	0.69	0.36	0.31
$NHC(O)CH_3$	0.14	-0.07	-0.27
$NH\text{-}NH_2$	-0.60	-0.08	-0.55
N=N-Ph	0.67	0.20	0.20
N=O	0.58	0.31	0.37
NO_2	0.87	0.20	0.35
$P(O)(OMe)_2$	0.48	0.16	0.24
$SiMe_3$	0.22	-0.02	-0.02
BPh_3^-	-0.16	-0.42	-0.56
F	-0.29	-0.02	-0.23
Cl	-0.02	-0.07	-0.13
Br	0.13	-0.13	-0.08
I	0.39	-0.21	0.00
OH	-0.53	-0.14	-0.43
OCH_3	-0.45	-0.07	-0.41

Paul Schatz, University of Wisconsin, Madison

J. Am. Chem. Soc. **1956**. *78*. 3043



$\delta_{Ar\text{-}H} = 7.36 + Z_{ortho} + Z_{meta} + Z_{para}$



δ = [7,36 + (2x0,13) - 0,14 - 0,08]

= 7,40