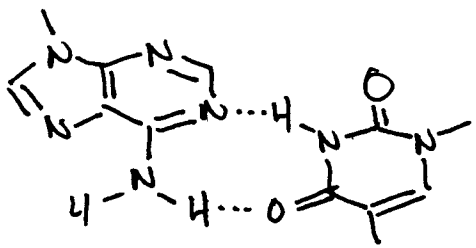
GREG BEUTNER

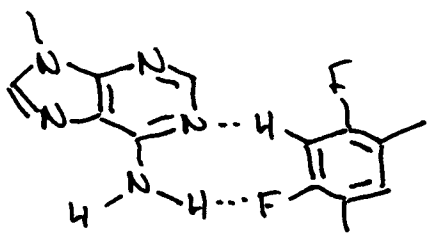
METAL - FLUORINE INTERACTIONS IN ORGANIC SYNTHESIS.

MARCH 27, 2001.



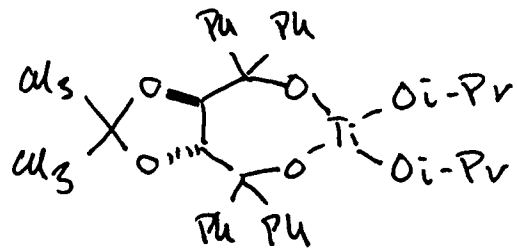
THYMIDINE A

VS.



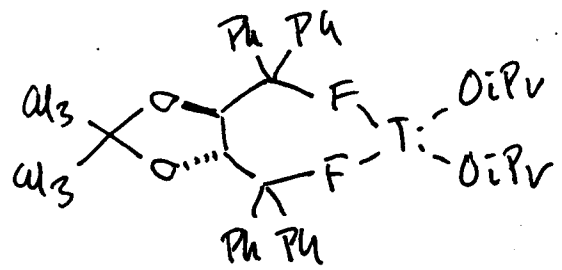
4,6-DIFLUORO-m-XYLENE B

$$K_{ASSOC}^{A} \times 0.6 = K_{ASSOC}^{B}$$



TADDOL C

VS.



F-TADDOL D

?

SHORT SIGHTED DISMISSAL OF METAL-FLUORINE INTERACTIONS?

- IF ONE CONSIDERS WHAT MAKES OXYGEN A GOOD DONOR LIGAND FOR METALS (ie HIGH ELECTRONEGATIVITY, LOW POLARIZABILITY), FLUORINE WOULD SEEM A LOGICAL, IF NOT SUPERIOR ALTERNATIVE.

ATOMIC PROPERTIES:

Element	IP (kcal/mol)	EA (kcal/mol)	CH_3-X (Å)	EN (Pauling)	r_v(Å) (Pauling)	r_v(Å) (Bondi)	BE CH_3-X (kcal/mol)
H	313.6	17.7	1.09	2.1	1.20	1.20	99
F	401.8	79.5	1.39	4.0	1.35	1.47	116
Cl	299.0	83.3	1.77	3.0	1.80	1.75	81
Br	272.2	72.6	1.93	2.8	1.95	1.85	68
O(OH)	310.4	33.7	1.43	3.5	1.40	1.52	86
S(SH)	238.9	48.0	1.82	2.5	1.85	1.80	65

IP, Ionization potential; EA, electron affinity; EN, electronegativity; BE, bond energy.

STERIC CONSIDERATIONS:

R	H	Me	*n*-Bu	*c*-Hex	CF_3	*i*-Bu	*s*-Bu	*t*-Bu	Ph
E_s	−1.24	0	0.39	0.79	1.16	0.93	1.13	1.54	–
E_s':	−1-12	0	0.31	0.69	0.78	0.93	1.00	1.43	2.31

E_s: Steric parameters suggested by K. W. Tafts.
E_s': Steric parameters suggested later by J.-E. Dubois.

FROM: HIYAMA, T. "ORGANOFLUORINE COMPOUNDS" pg. 2

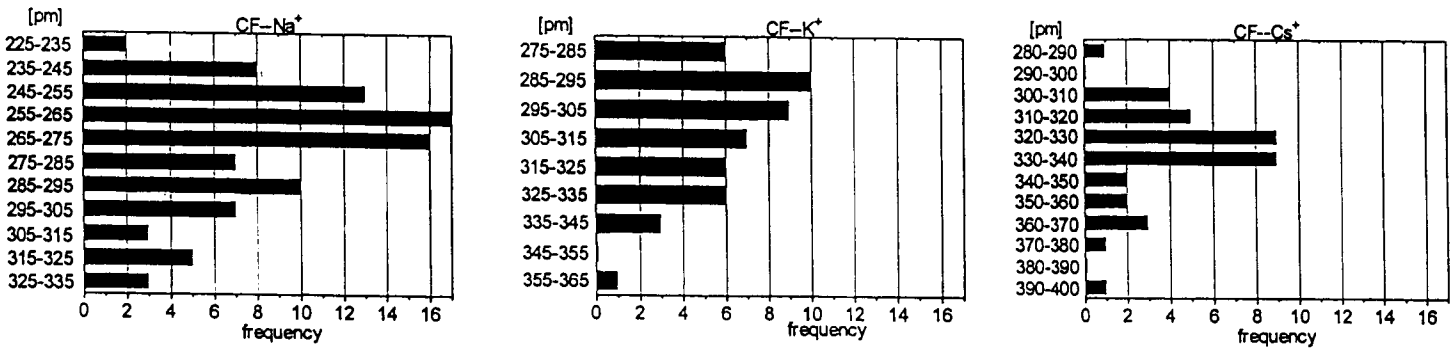
- ALSO:
  - ^1H ($I = 1/2$) ~ 100% NAT. ABUNDANCE — REL. SENSITIVITY 1
  - ^{13}C ($I = 1/2$) ~ 1% NAT. ABUNDANCE — REL. SENSITIVITY 0.0159
  - ^{17}O ($I = 5/2$) < 1% NAT. ABUNDANCE — REL. SENSITIVITY 0.0291
  - ^{19}F ($I = 1/2$) ~ 100% NAT. ABUNDANCE — REL. SENSITIVITY 0.834

PLUS: 250 ppm δ WINDOW, EXTREMELY SHORT T_1'S!

FLUORINE MAY PROVIDE A NOVEL ALTERNATIVE

X-RAY STRUCTURE SEARCH REVEALS PATTERNS IN C-F··M

ANALYSES OF THE CAMBRIDGE STRUCTURAL DATA BASE REVEALED REGULARITIES IN C-F-M BOND LENGTHS.



A NUMBER OF METALS ACROSS THE PERIODIC TABLE HAVE KNOWN M-F CONTACTS:

Li, Na, K, Rb, Cs, Ca, Sr, Ba, Sc, Zn, Y, Zr, Cd, Ag, La, Hg, Al, Ga, In
Tl, Ge, Sn, Pb AND Bi

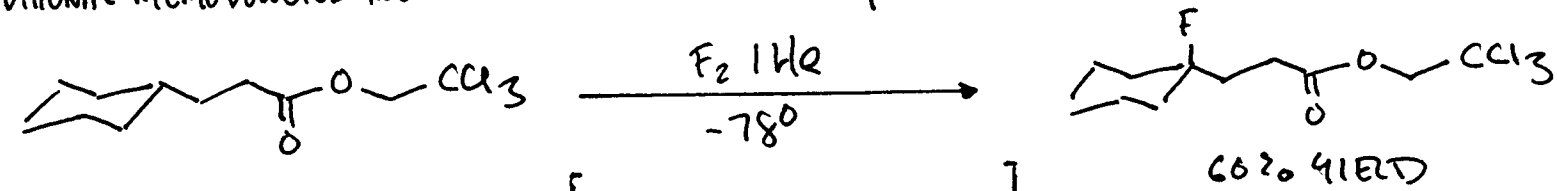
PLENIO, H. CHEM REV. (1997) 97 3363.

THERE MAY BE WAY MORE C-F··M BONDS THAN WE THINK

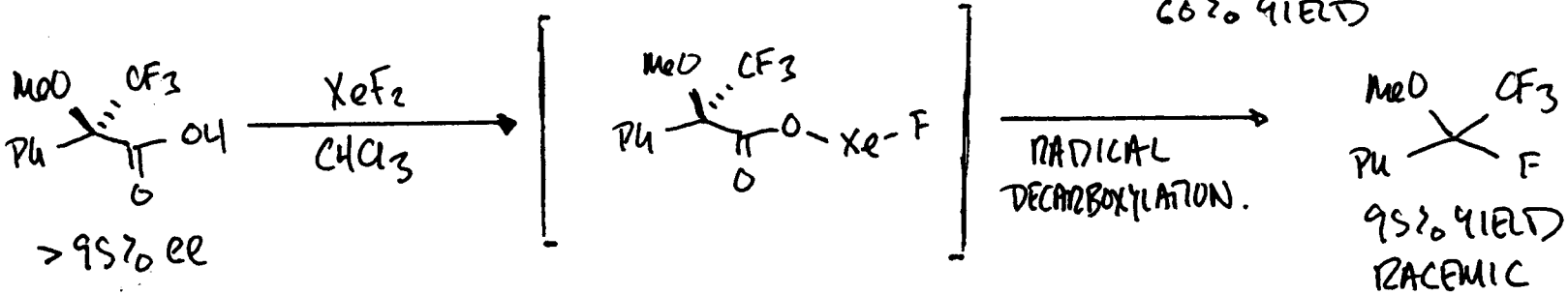
WHERE DO FLUORINES COME FROM?

- TRADITIONAL METHODOLOGIES ARE NOT SO USER FRIENDLY:

(1)



(2)



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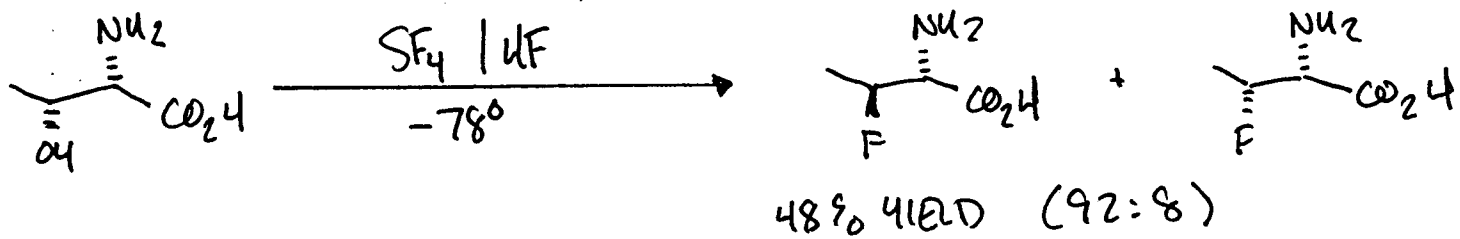
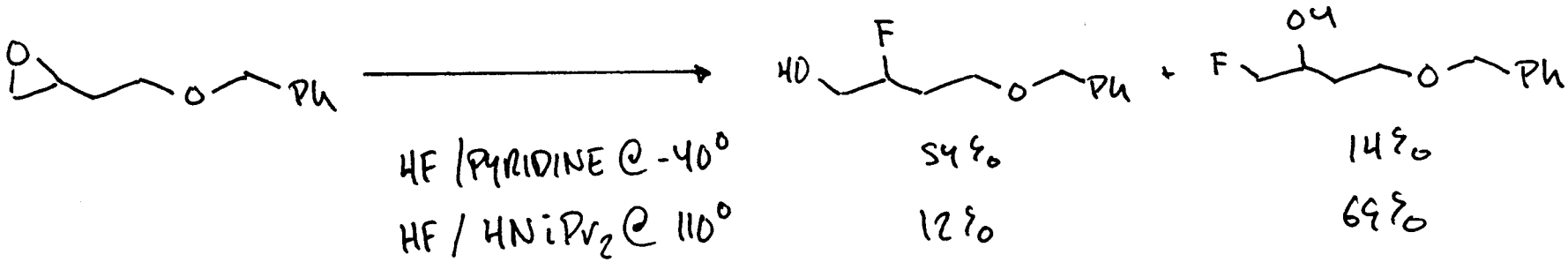


(4)

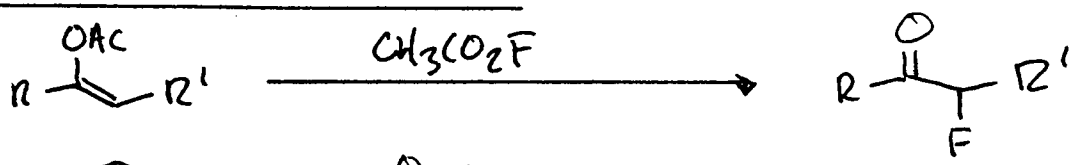


EARLY METHODS WERE HARSH, SENSITIVE AND UNSELECTIVE PROCESSES.

WHERE DO FLUORINES COME FROM NOW?

ELECTROPHILIC FLUORINATING REAGENTS:

(1)

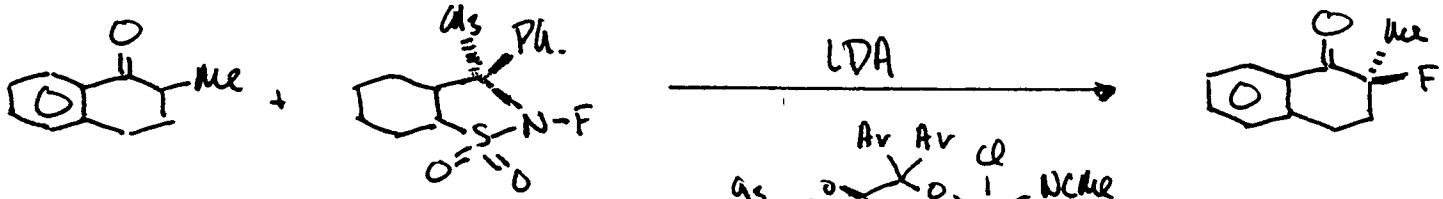


> 80% YIELD.

(2)

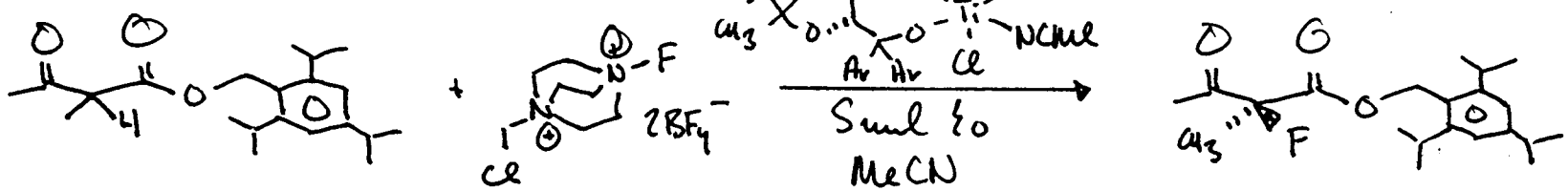
81% YIELD.

(3)



81% YIELD
80% ee

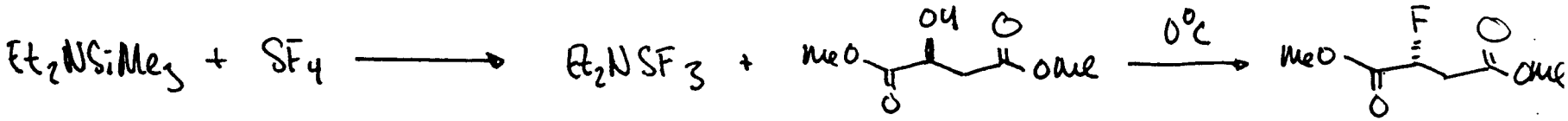
(4)



85% YIELD | 90% ee

NUCLEOPHILIC FLUORINATING REAGENTS:

(1)

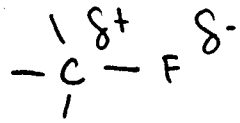


85% YIELD.

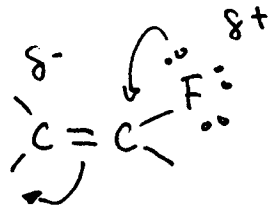
N-F AND O-F COMPOUNDS HOLD THE KEY TO EASY INSTALLATION OF FLUORINE

EFFECTS OF FLUORINE SUBSTITUTION ON REACTIVE CENTERS

○ FLUORINE:



$-I_\sigma$ EFFECT.



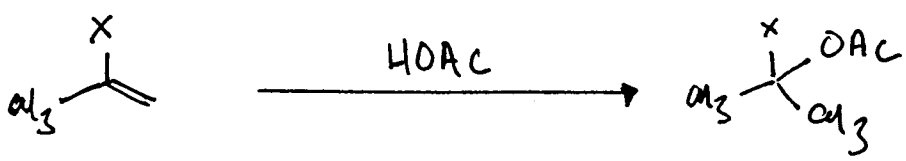
$+I_\pi$ EFFECT

BALANCE OF THESE 2 EFFECTS IS CRUCIAL:

$\sigma_{m(F)} = 0.34$ $\sigma_{p(F)} = 0.06$

CATIONS:

FLUORINE TENDS TO STABILIZE α CATIONS (PREDOMINANCE OF $+I_\pi$) AND DESTABILIZE MORE REMOTE CATIONS.



$K_F >> K_{Cl} > K_{Br} > K_H$

ANIONS:

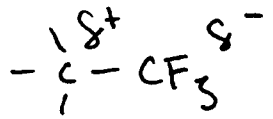
FLUORINE TENDS TO DESTABILIZE α ANIONS (PREDOMINANCE OF $+I_\pi$) AND STABILIZE MORE REMOTE ANIONS.

Acid	pK_a (25°C)	Acid	pK_a (25°C)
CHF_3	30.5	CF_3CHF_2	28.2
$CHCl_3$	24.4	CF_3CHCl_2	24.4
$CHBr_3$	22.7	CF_3CHBr_2	23.7
CHI_3	22.5	CF_3CHI_2	24.1
CH_3CO_2H	4.8	CH_3SO_3H	−1.9
CH_2FCO_2H	2.6	CF_3SO_3H	−5.1
CHF_2CO_2H	1.2	$C_6H_5CO_2H$	4.2
CF_3CO_2H	0.2	$C_6F_5CO_2H$	4.4
CH_2ClCO_2H	2.9	C_6H_5OH	9.9
$CHCl_2CO_2H$	1.3	C_6F_5OH	5.5
CCl_3CO_2H	0.6	C_6Cl_5OH	5.3

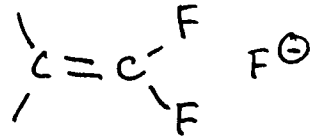
SUBSTITUTION BY FLUORINE CAUSES UNIQUE RESULTS

EFFECTS OF FLUORINE SUBSTITUTION ON REACTIVE CENTERS.

○ TRIFLUOROMETHYL:



$-I_\sigma$ EFFECT

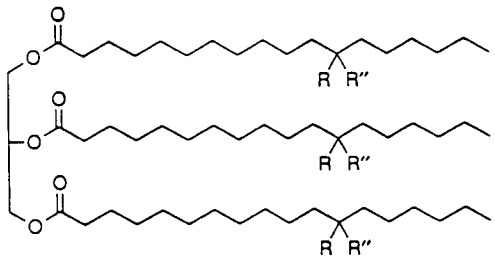


NEGATIVE HYPERCONJUGATION.

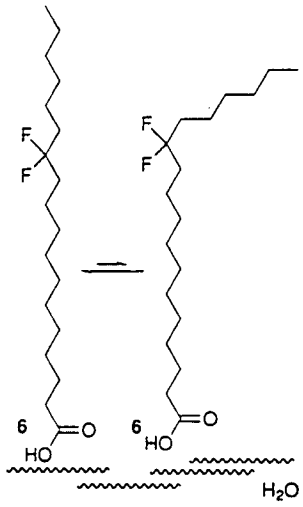
NO CONTRADICTORY I_π EFFECT:

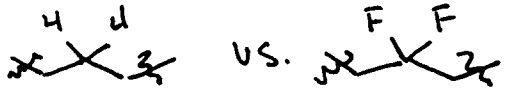
$\sigma_m(CF_3) = 0.43 \quad \sigma_p(CF_3) = 0.54$

○ STRUCTURAL EFFECTS:



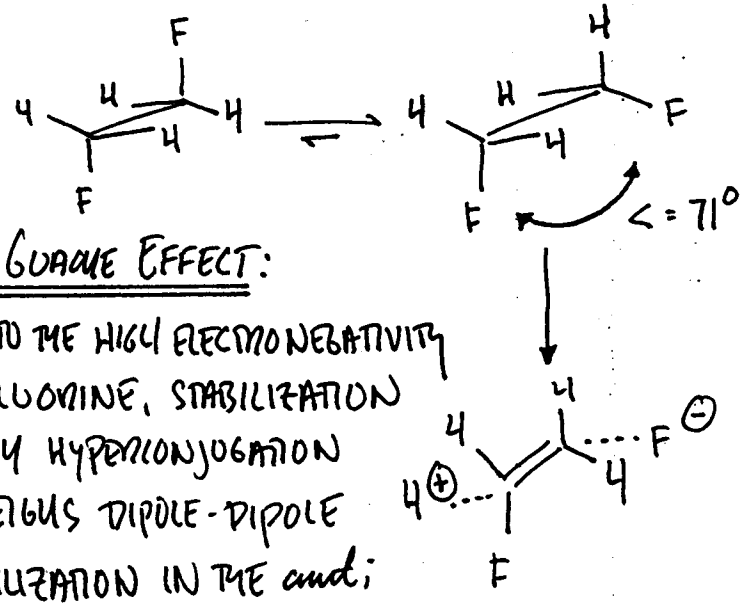
1 R = R'' = H mp = 72 °C
2 R = H, R'' = F mp = 73 °C
3 R = R'' = F mp = 58 °C





$\angle C\text{-}CH_2\text{-}C \sim 109°$ vs. $\angle C\text{-}CF_2\text{-}C \sim 116°$

anti: gauche.



$\angle = 71°$

THE GUAUCHE EFFECT:

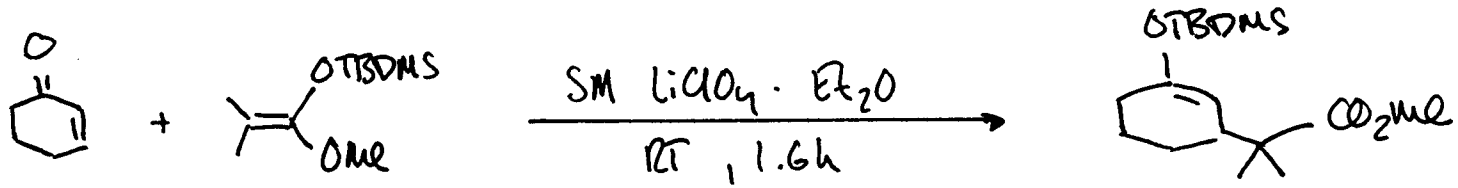
DUE TO THE HIGH ELECTRONEGATIVITY OF FLUORINE, STABILIZATION THROUGH HYPERCONJUGATION OUTWEIGHS DIPOLE-DIPOLE STABILIZATION IN THE anti FORM.

O'HAGAN, D.; PZEPA, H.S. JCS CHEM COMM (1997) 645.

FLUORINE AS A WEAKLY COORDINATING ANIONIC LIGAND

- $Li(ClO_4)$ IS A POWERFUL LEWIS ACID CATALYST FOR DIELS-ALDER REACTIONS, MICHEAL ADDITIONS + ALDOLS IN NON-COORDINATING SOLVENT (TYP. DCE)
- INDUSTRIALLY THIS IS IMPRACTICAL.

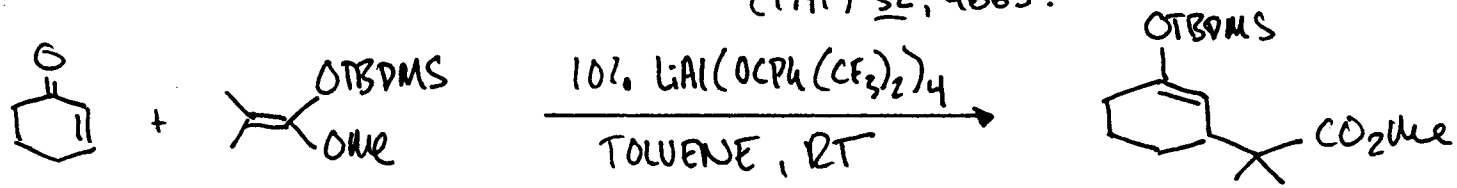
(1)



76% YIELD

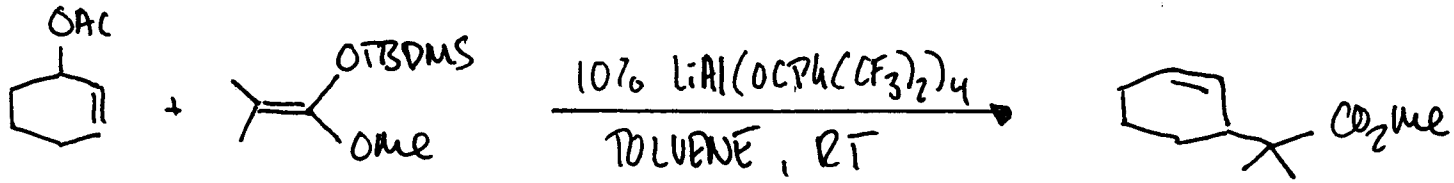
GRIECO, P.A.; COOKE, R.J.; HENRY, K.J.; VANDER ROEST, J.M TETRAHEDRON LETT (1991) 32, 4665.

(2)



97% YIELD.

(3)



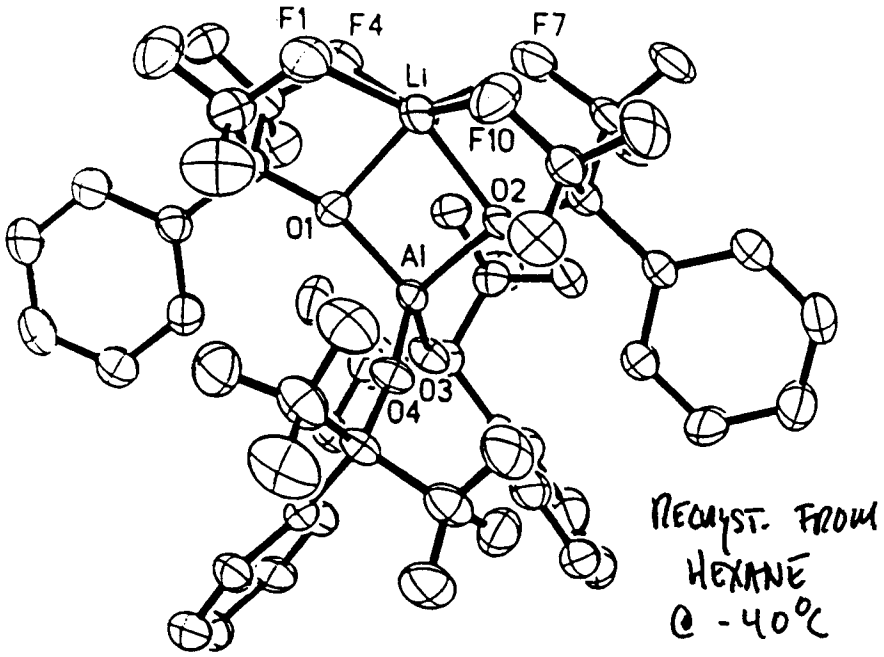
92% YIELD.

GRIECO, D.A, et al. ORGANOMETALLICS (1996) 15, 3776.

THE TRIFLUOROMETHYL GROUP ACTS AS A SURROGATE FOR $ClO_4^{\ominus}$

EVIDENCE FOR THE ROLE OF THE FLUORINES.

THIS MATERIAL IS HYGROSCOPIC + VOLATILE. PURIFICATION BY VAC. SUBLIMATION IS STRAIGHTFORWARD.



RECRYST. FROM HEXANE @ -40°C

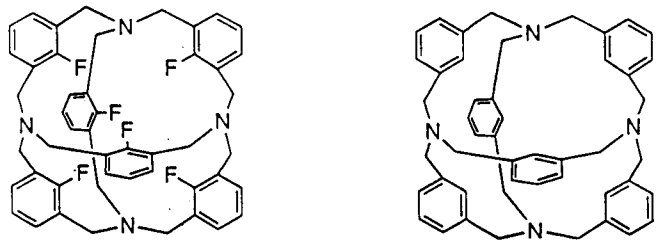
$$HOC(CF_3)_2Ph \xrightarrow[\text{TOLUENE}]{\text{LiAlH}_4} LiAl(OC(CF_3)_2Ph)_4$$

- THE LiO_2F_4 FRAGMENT IS TRI. PRISMATIC.
- C-F··Li BOND LENGTHS 1.98 – 2.35 Å. THIS IS THE SHORTEST Li-F CONTACT ON RECORD. THE VALUES ARE EQUAL WITHIN $\pm 3\sigma$.
- COORDINATED C-F BONDS ARE LENGTHENED ca. 0.5 Å RELATIVE TO UNCOORDINATED BONDS

^{19}F SPECTROSCOPY SHOWS A COMPLEX PATTERN AT -75.9 ppm. IT IS A 1:1:1:1 QUARTET SUPERIMPOSED ON A BROAD SINGLET. THIS IS AS EXPECTED FOR COORDINATION OF 4 EQUIV. FLUORINES TO 1 LITHIUM ATOM ($I = 3/2$ FOR ^7Li (92.5 % NA) AND $I = 1$ FOR ^6Li (7.5 % NA)).

FLUORINES ATOMS SERVE TO RELEASE THE NAKED Li^+ INTO SOLUTION

FINDING FLUORINE · METAL INTERACTIONS: ^{19}F NMR



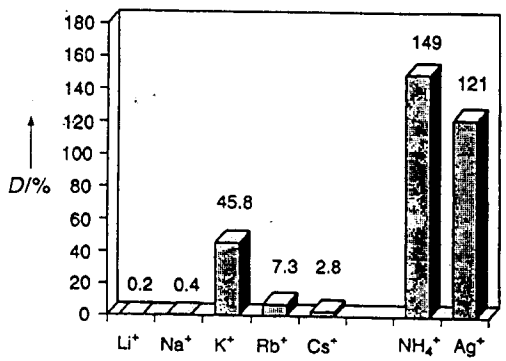


Figure 1. Distribution ratios $D[\%]$ of metal picrates. $D[\%] = [Pic^-]_{org}/([Pic^-]_i - [Pic^-]_{org}) \times 100$; $[Pic^-]_i$ is the initial concentration of picrate in the aqueous phase, and $[Pic^-]_{org}$ is the observed concentration of picrate in the organic phase. Ligand 1: 1.0×10^{-3} M in chloroform; the metal picrates are formed from 0.10 M metal chloride or nitrate (Ag^+) and 1.01×10^{-3} M lithium picrate.

TAKEMURA, H.; et al ACIEE (1999) 38, 959.

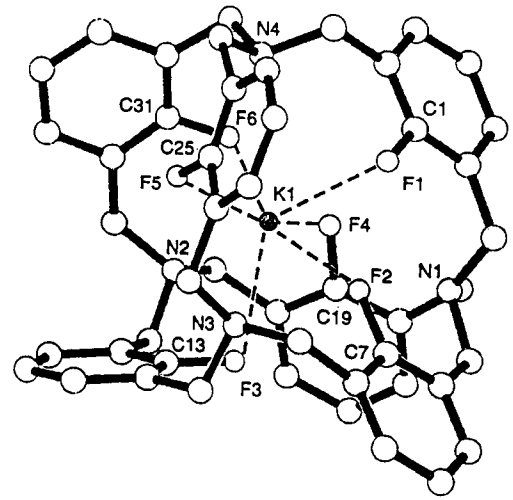


Figure 2. Crystal structure of $K^+ \subset 1$ (H atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: K1–F1 2.920(3), K1–F2 2.563(3), K1–F3 2.786(3), K1–F4 2.704(3), K1–F5 2.727(3), K1–F6 2.722(3), K1–N1 3.739(4), K1–N2 3.276(4), K1–N3 3.629(4), K1–N4 3.295(4); C1-F1-K1 95.1(2), C7-F2-K1 148.2(3), C13-F3-K1 105.4(2), C19-F4-K1 116.2(2), C25-F5-K1 109.9(2), C31-F6-K1 98.4(2).

^{19}F NMR: $\delta = -110.50$ ppm (LIGAND) $^1J_{CF} = 260.5$ Hz

$\delta = -126.26$ ppm (LIGAND · K^+) $^1J_{CF} = 247.8$ Hz

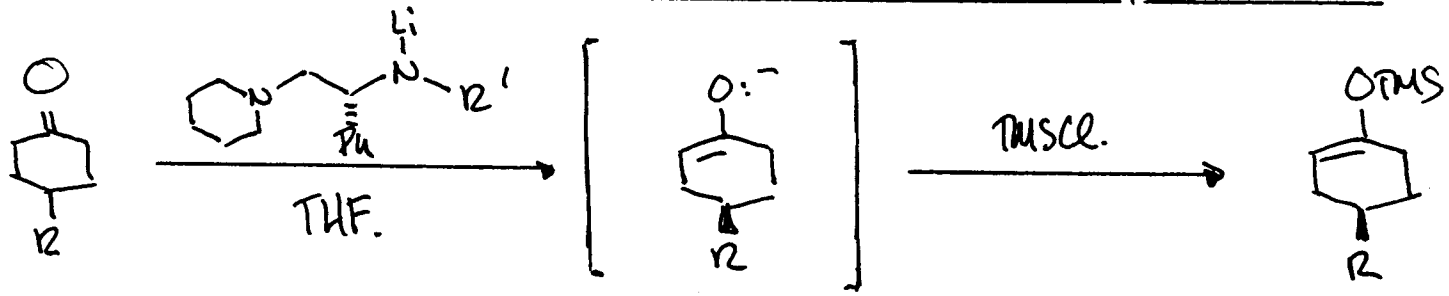
X-RAY: F2, F4, F5 + F6 ARE COPLANAR

$\bar{r}_{K-F} = 2.74$ Å $r^{min}_{K-F} = 2.56$ Å

ALSO, SHORTER C-F-K CONTACTS ARE MORE LINEAR.

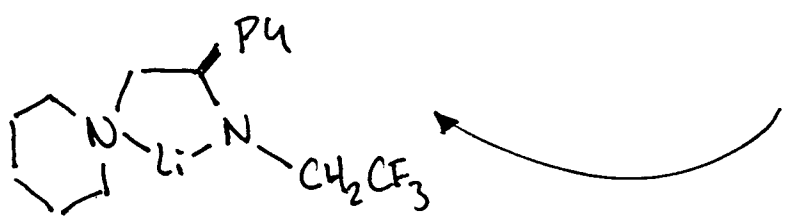
NMR IS A GOOD TOOL FOR IDENTIFYING FLUORINE INTERACTIONS

EFFECT OF FLUORINATION ON CHIRAL AMINE BASES IN DESYMMETRIZATION.



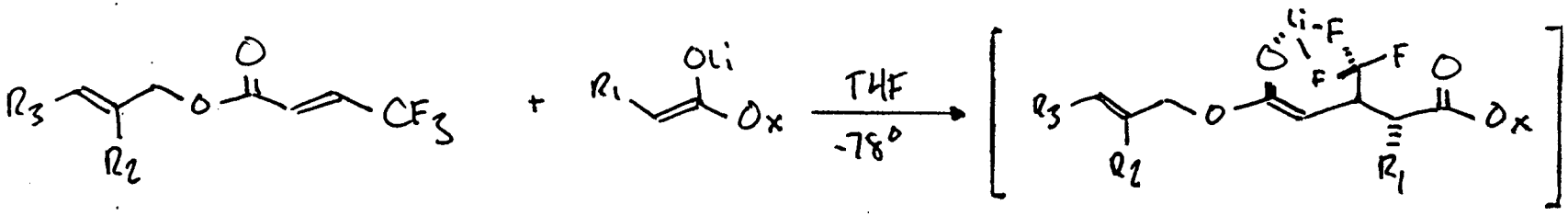
Run	Ketone 1	Ketone R	Lithium amide (R)-2	Lithium amide R	HMPA (eq.)	Temp. (°C)	Product (R)-4	Product Chem. y. (%)	Product Optical y. (%)
1	1a	Bu^t	2a	CH_2CH_3	0	-78	4a	86	52
2	1a	Bu^t	2a	CH_2CH_3	1.2	-78	4a	93	78
5	1a	Bu^t	2c	$CH(CH_3)_2$	0	-78	4a	87	65
6	1a	Bu^t	2c	$CH(CH_3)_2$	1.2	-78	4a	73	75
7	1a	Bu^t	2d	CH_2Bu^t	0	-78	4a	93	86
8	1a	Bu^t	2d	CH_2Bu^t	1.2	-78	4a	94	84
9	1a	Bu^t	2e	CH_2CH_2F	0	-78	4a	85	69
10	1a	Bu^t	2e	CH_2CH_2F	1.2	-78	4a	67	85
11	1a	Bu^t	2f	CH_2CHF_2	0	-78	4a	93	77
12	1a	Bu^t	2f	CH_2CHF_2	1.2	-78	4a	92	89
13	1a	Bu^t	2g	CH_2CF_3	0	-78	4a	88	84
14	1a	Bu^t	2g	CH_2CF_3	1.2	-78	4a	74	87
21	1b	Ph	2g	CH_2CF_3	1.2	-100	4b	95	93
22	1c	Pr^i	2g	CH_2CF_3	1.2	-100	4c	92	95
23	1d	Me	2g	CH_2CF_3	1.2	-100	4d	76	94

- ENANTIOSELECTIVITY INCREASES WITH BOTH THE STERIC DEMAND + DEGREE OF FLUORINE SUBSTITUTION IN R.
- HMPA DOES NOT SERIOUSLY AFFECT THE HIGHLY SELECTIVE CASES.
- NMR (^{15}N, ^{7}Li + ^{19}F) DO NOT INDICATE ANY Li-F BONDING.
- "IT IS CONCEIVABLE THAT ELECTROSTATIC INTERACTION BETWEEN δ^- OF THE FLOURINE AND δ^+ OF THE LITHIUM FIXES THE CONFORMATION OF THE CHELATED MONOMERIC FORM OF 2e-h."

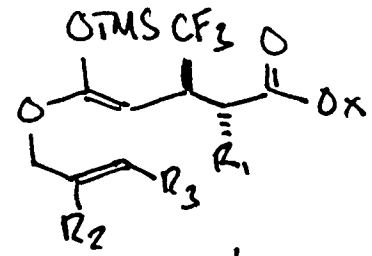


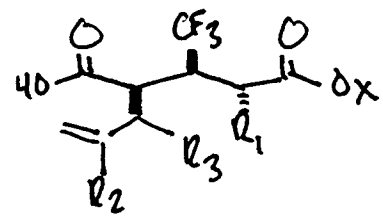
MOGA, N; et al TETRAHEDRON LETT (1993) 34, 5105.

FLUORINE - METAL INTERACTIONS INHIBIT RETRO-MICHAEL ADDITION



- REPLACEMENT OF CF_3 WITH CH_3 LEADS TO LOWER YIELDS AND DIASTEREOSELECTIVITY (de 64%).





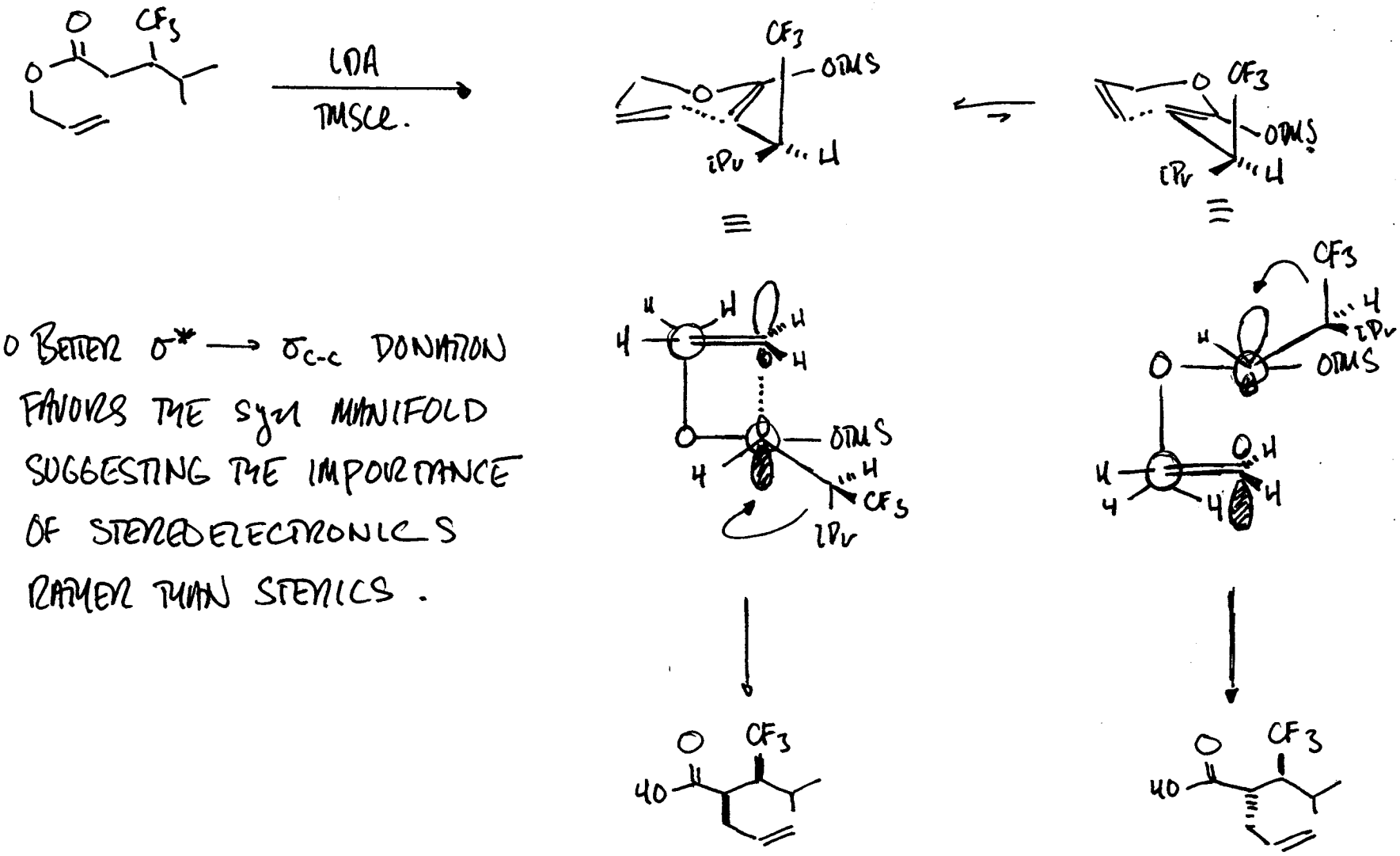
entry	acceptor	R^1	R^2	R^3	product	isolated yield[b] (%) 3	4
1[d]	1a	Me	H	H	3a	55	22
2	1a	Me	H	H	3a	65 (44)	22 (45)
3[e]	1a	Me	H	H	3a	47	16
4	1a	Et	H	H	3b	63	32
5	1a	*i*-Pr	H	H	3c	60	32
6	1b	Me	Me	H	3d	65	21
7	1b	Et	Me	H	3e	74	34[c]
8	1b	*i*-Pr	Me	H	3f	62	45[c]
9	1c	Me	H	Me	3g	0	79

[a] The Ireland–Claisen rearrangement was carried out at reflux for 6 h after addition of a Pd(II) catalyst to ketene silyl acetal obtained *in situ*. [b] The yields obtained in the absence of a Pd(II) catalyst are shown in parentheses. [c] These yields were determined by ^{19}F NMR with $PhCF_3$ as an internal standard. [d] Reflux for 4 h. [e] Reflux for 11 h.

SATO, S; et al JOC (1995) 60 8140.

> 98% de BY NMR.

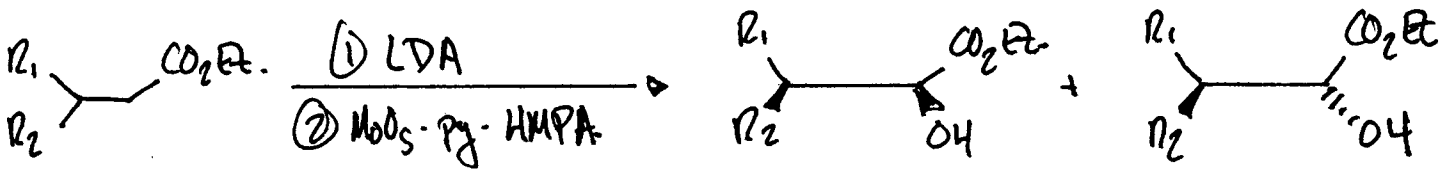
STEREO-ELECTRONIC EFFECTS IN THE IRELAND CLAISEN REARRANGEMENT



- BETTER $\sigma^* \longrightarrow \sigma_{C-C}$ DONATION FAVORS THE syn MANIFOLD SUGGESTING THE IMPORTANCE OF STEREOELECTRONICS RATHER THAN STERICS.

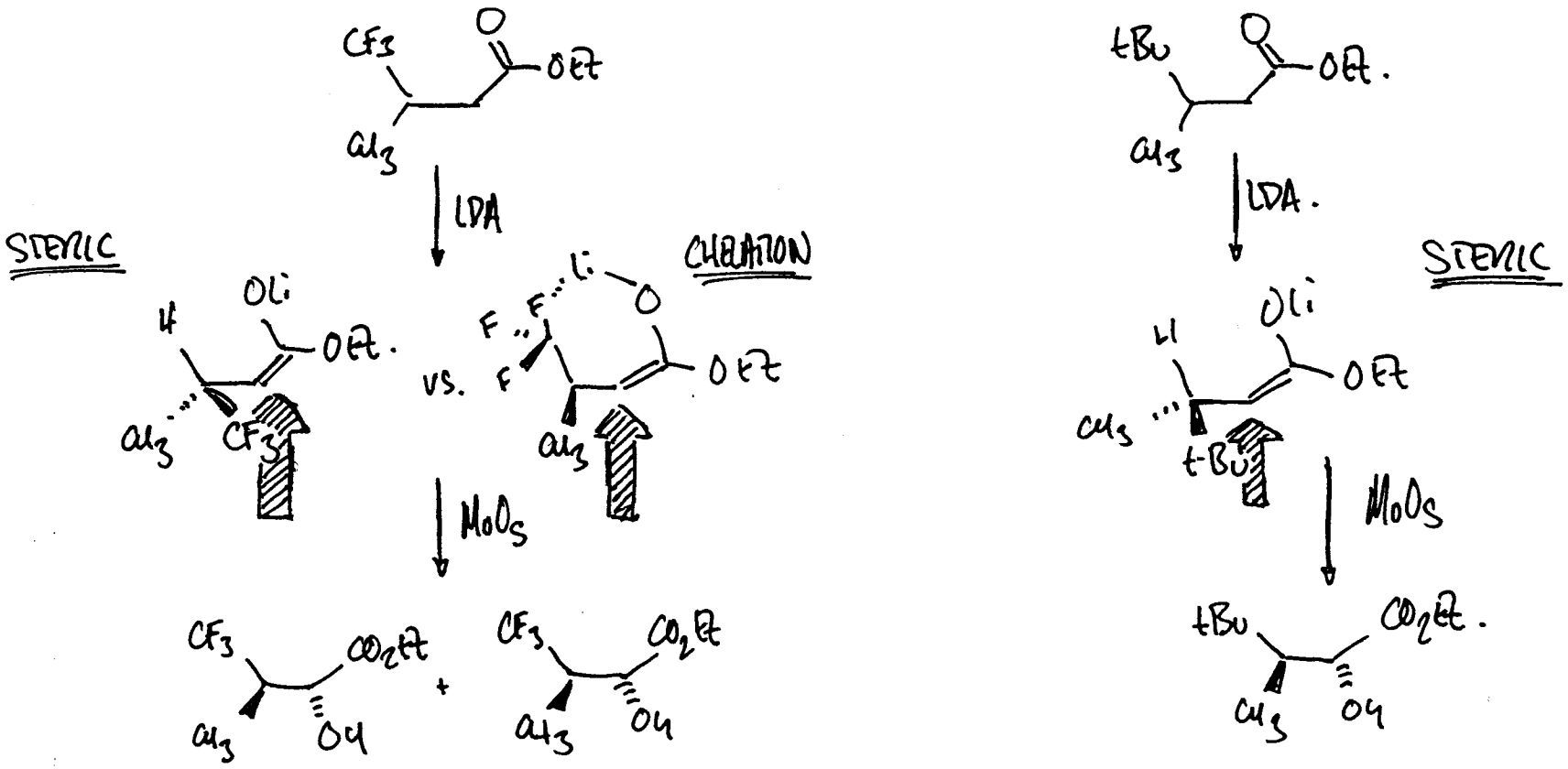
71% YIELD
82:18 syn : anti

Unusual Diastereoselectivity in Enolate α-Hydroxylation?

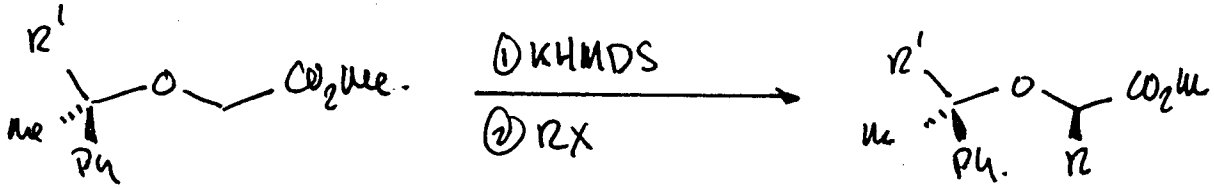


R_1	R_2	YIELD	A	:	B
CF_3	CH_3	58%	3		97
CFH_2	CH_3	60%	37		63
t-Bu	CH_3	45%	<5		>95

Morizawa, Y; et al Tetrahedron Lett (1986), 1833.



FLUORINE CONTAINING CHIRAL AUXILIARIES

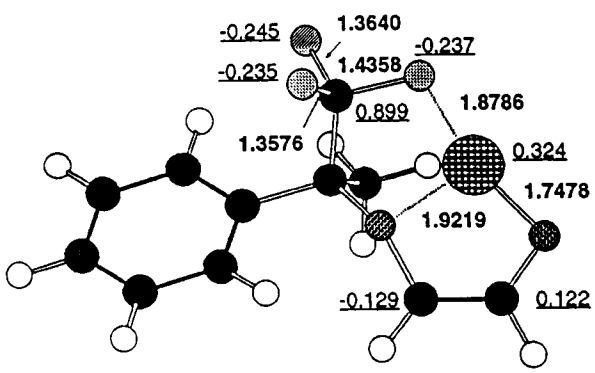


YAMAZAKI, T; et al Org. Lett (1999) 1, 905.

R'	isolated yield (%) [DS, % de] MeI	PhCH₂Br	allyl-I	steric factors[a] Es	Es'
CF_3 (1a)	67 [90]	79 [80]	82 [68]	−1.16	−0.78
CHF_2 (1b)	58 [88]	45 [84]	61 [72]	−0.67	−0.32
CH_2F (1c)	50 [82]	41 [84]	49 [62]	−0.24	−0.20
i-Pr (1d)	50 [56]	31 [48]	77 [28]	−0.47	−0.48

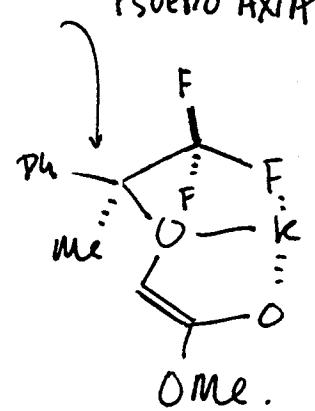
[a] Es: Taft steric constant with reference to a methyl group (Me: 0.00). Es': revised Taft steric constant by Dubois and co-workers. Me: 0.00. Ph: −2.31.

- TRENDS IN DIASTEREOSELECTIVITY DO NOT MATCH WELL WITH TAFT Es PARAMETERS SUGGESTING SIMPLE STERIC DIFFERENTIATION IS NOT ENOUGH.



MB3LYP/3-216

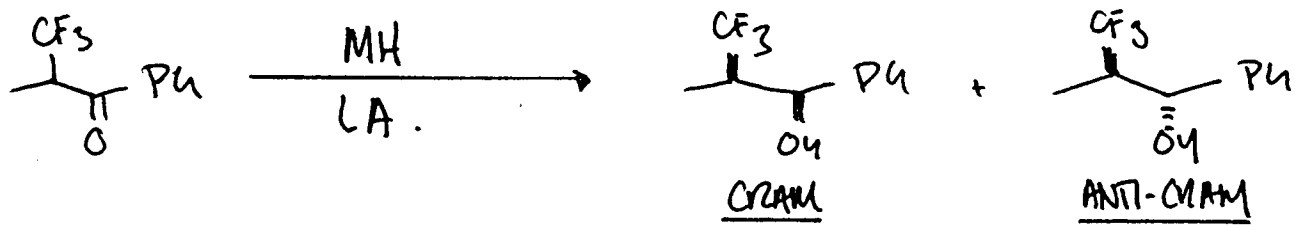
PSUEDO AXIAL METHYL GROUP PROVIDES STERIC BIAS.



ΔE BETWEEN THE 2 LOWEST ENERGY CONFORMERS IS 0.81 kcal/mol WHICH CORRELATES TO A SELECTIVITY OF 94.6:5.4 @ -78°C.

ENOLATE GEOMETRY FIXED BY F-K INTERACTION

SUBSTRATE DIRECTED REDUCTION OF KETONES BY METAL HYDRIDES



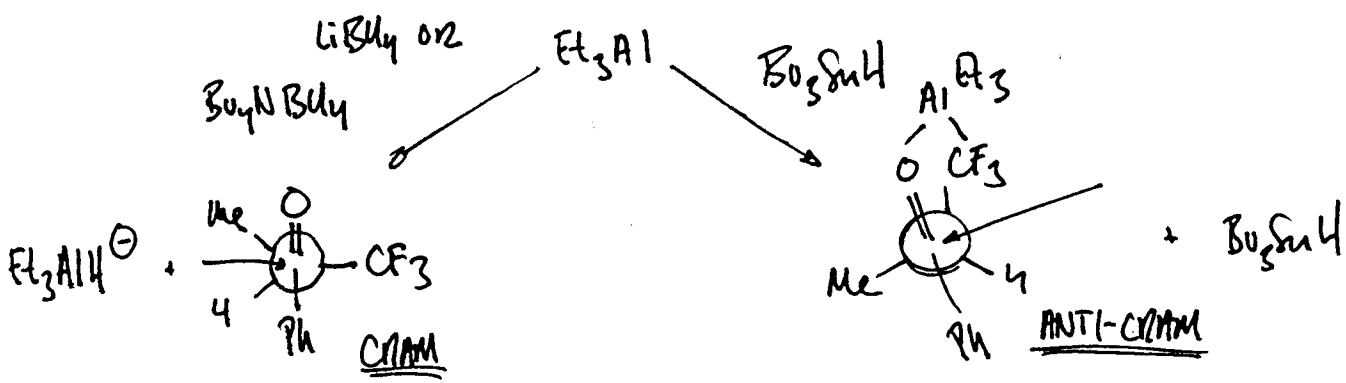
entry	Lewis acid	solvent	temp (°C)	Cram:anti-Cram[a]	yield (%)
1	none	CH_2Cl_2	−78–rt[d]	69:31	91
2	none	Et_2O	−78–rt	77:23	88
3	none	THF	−78–rt	66:34	60
4	$ZnCl_2$	Et_2O	−78–rt	87:13	85
5	$SnCl_4$	CH_2Cl_2	−78–rt	65:35	89
6	$SnCl_4$	Et_2O	−78–rt	90:10	83
7	Et_3Al	CH_2Cl_2	−78–rt	76:24	64
8	Et_3Al	Et_2O	−78–rt	96:4	86
9	Et_3Al	CH_2Cl_2	−78–rt	97:3	89[b]
10	$TiCl_4$	CH_2Cl_2	−78–rt	69:31	47
11	$TiCl_4$	Et_2O	−78–rt	98:2	49
12	$MeAlCl_2$	CH_2Cl_2	−78–rt	79:21	62
13	$MeAlCl_2$	CH_2Cl_2	−78–rt	89:11	69[c]
14	$MeAlCl_2$	Et_2O	−78–rt	99:1	75
15	$MeAlCl_2$	THF	−78–rt	86:14	68

[a] Isomeric ratio by HPLC. Reductions were conducted at by using 1.5 equiv of Lewis acid and 5 equiv of $LiBH_4$. [b] Reduction was conducted by using 1.5 equiv of Lewis acid and 5 equiv of Bu_4NBH_4. [c] In the presence of 12-crown-4. [d] rt = room temperature.

entry	Lewis acid	solvent	temp (°C)	Cram:anti-Cram[a]	yield (%)[b]
1	none	CH_2Cl_2	−78–rt[c]		no reactn
2	Me_3Ga	CH_2Cl_2	−78–rt	73:27	57
3	$TiCl_2(O^iPr)_2$	CH_2Cl_2	−78–rt	72:28	87
4	$MeAlCl_2$	CH_2Cl_2	−78–rt	64:36	70
5	Et_2AlCl	CH_2Cl_2	−78–rt	48:52	72
6	Et_2AlCN	CH_2Cl_2	−78–rt	36:64	50
7	Et_3Al	CH_2Cl_2	−78–rt	32:68	71
8	Et_3Al	hexane	−78–rt	25:75	67 (93)
9	Et_3Al	toluene	−78–rt	15:85	64 (94)
10	Me_3Al	toluene	−78–rt	13:87	(92)

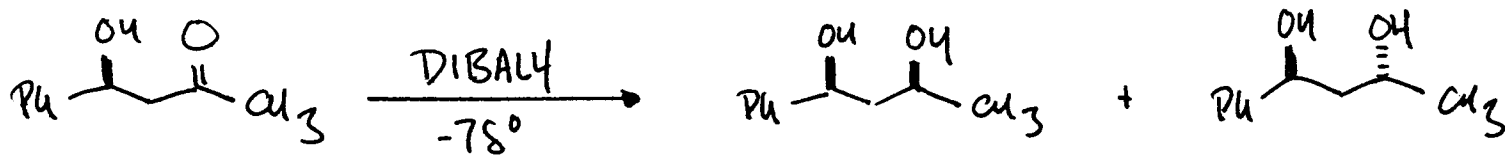
[a] Isomeric ratio by HPLC. Reductions were conducted by using 2 equiv of Lewis acid and 4 equiv of Bu_3SnH. [b] GC yield in parentheses. [c] rt = room temperature.

FUCHIKAMI, T; et al JOC (1990) 55, 4969.

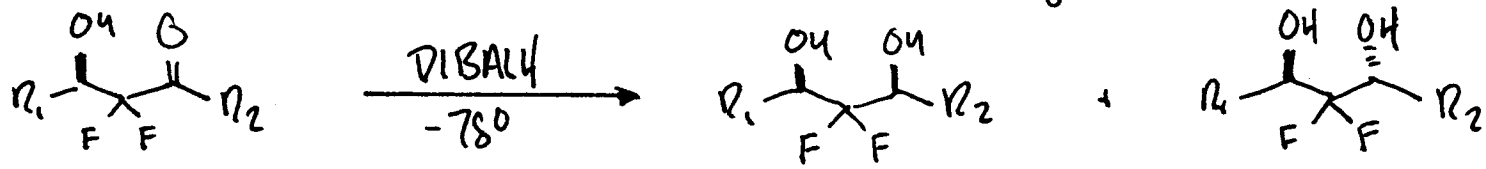


INTRAMOLECULAR CHELATION AFFECTS REACTIVE CONFORMATION.

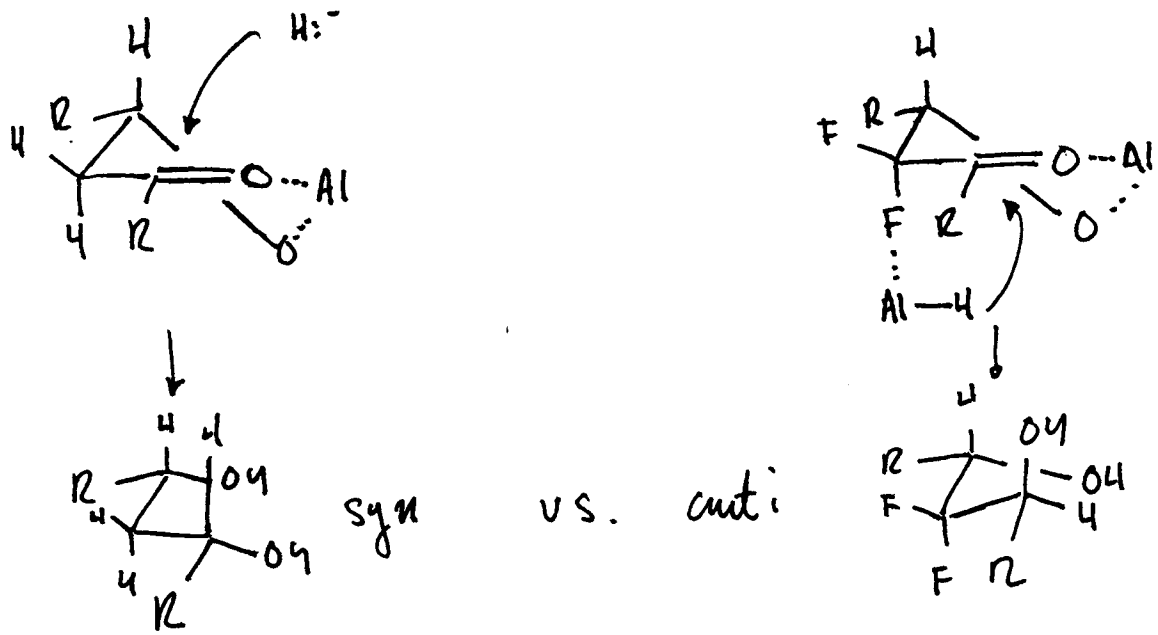
Substrate Directed Reduction of Ketones by Metal Hydrides.



95:5 syn : anti

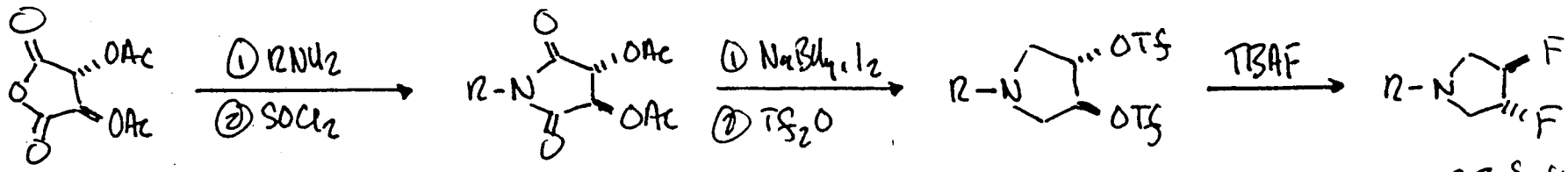


R_1	R_2	YIELD	syn	:	anti
Ph	Ph	99%	0	:	100
Ph	n-C_6H_{13}	95%	25	:	75

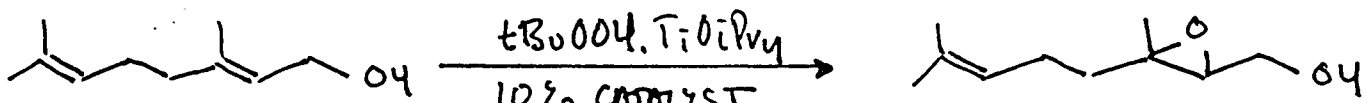


Ishihara, T; et al Bull Chem Soc Jpn (1990) 63, 1185.

FLUORINATED LIGANDS IN ASYMMETRIC EPOXIDATIONS.

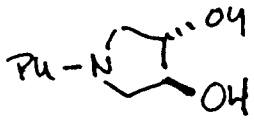


76-83 % y.



Entry	Catalyst	T/°C	t/h	Yield (%)	Ee (%)	Configuration
1	—	−20 to 20	12	81	—	racemic
2	3a	−20 to −10	0.67	97	25	(S,S)
3	5b	−20 to 20	1	68	50	(R,R)
4	5b	0	1	74	51	(R,R)
5	5b	−20 to 20	12	90	66	(R,R)
6	5b	−80	3	23	27	(R,R)
7	5c	−20 to 20	12	87	10	(R,R)

3a :



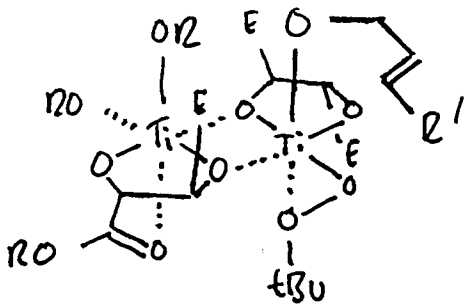
5b : R = n-C_8H_{17}

5c : R = Chx

MARSON, C.M.; MELLING, R.C. JCS CHEM COMM (1998) 1223.

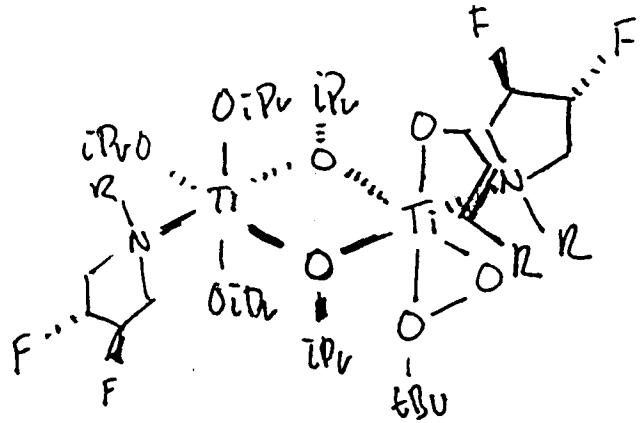
SELECTIVITY OBTAINED WITH THE FLUORINATED LIGAND IS SUPERIOR

PROPOSED CATALYSTS + INTERACTIONS.



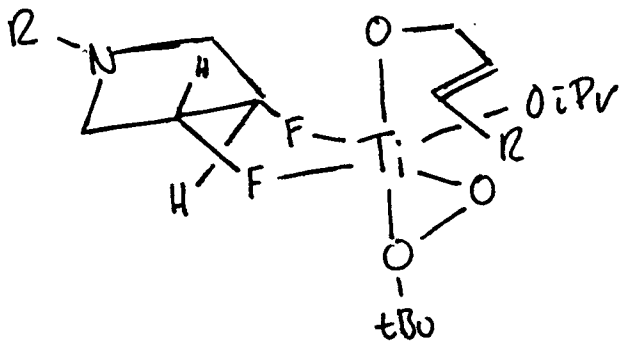
SHARPLESS TRANSITION STATE

1



NITROGEN COORDINATION

2

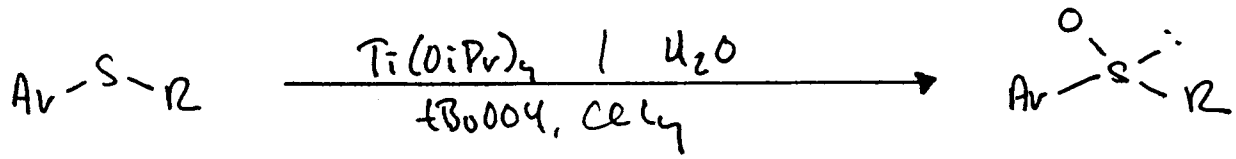


FLUORINE BIDENTATE COORDINATION

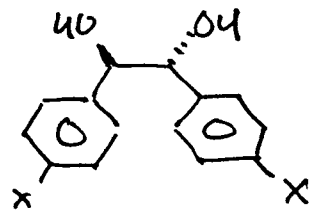
3

SYSTEM IS UNDERDEFINED TO DRAW REASONABLE STRUCTURES.

FLUORINATED LIGANDS IN ASYMMETRIC SULFIDE OXIDATIONS.



R = TOLYL (2a)
R = Bu (2b)



X = H (1a)
= OMe (1b)
= CF_3 (1c)

Table. Enantioselective oxidations employing diols (*R,R*)-1a-c as ligands[a]

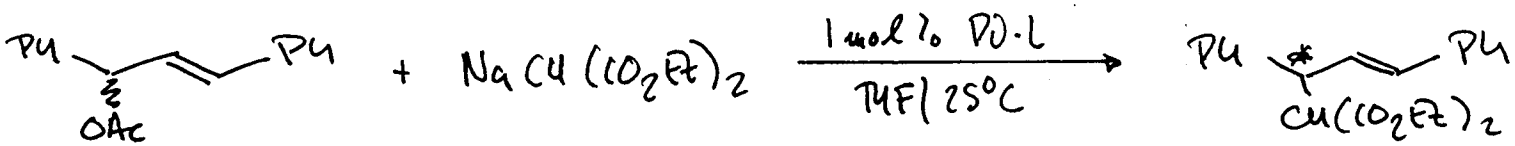
entry	diol	sulfide	sulfoxide (%)[b]	ee (%)	Abs. conf.[c]
1	1a	2a	62	80[d]	*S*
2	1a	2b	73	99[e]	*S*
3	1b	2a	60	48[d]	*S*
4	1b	2b	65	92[e]	*S*
5	1c	2a	70	26[d]	*R*
6	1c	2b	80	18[e]	*S*

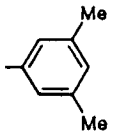
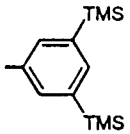
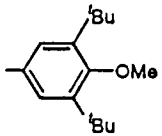
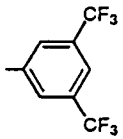
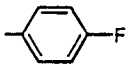
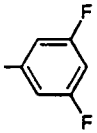
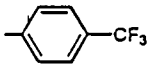
[a] Conditions: sulfide/(*R,R*)-1/Ti(*i*-PrO)$_4$/H_2O = 1.0/0.1/0.05/1.0 in CCl_4 at 0°C under N_2 atmosphere, reaction time 2 h, 2 equivalents of 70% TBHP in water as oxidant. [b] Isolated yields, amount of sulfone < 10%. [c] Determined by comparison of $[\alpha]_D$ with literature values, see ref. 15 [d] Determined by HPLC on a Daicel Chiralcel OB column. [e] Determined by HPLC on a Daicel Chiralcel OJ column.

- ALTHOUGH THE SURVEY IS NOT EXTENSIVE, EDG GROUPS SEEM TO LOWER SELECTIVITY WHILE EWG GROUPS INCREASE IT. DUE TO THE REMOTE POSITION OF THE CF_3, DIRECT COORDINATION SEEMS UNLIKELY.

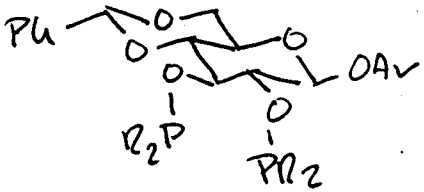
ROSINI, C.; et al (1998) 39 TETRAHEDRON LETT 8541.

FLUORINATED LIGANDS IN PALLADIUM CATALYZED ALLYLIC ALKYLATION.



entry	R[a]	^{31}P NMR, ppm[b]	ee, %[c]	config.[d]
1	Ph	118.6, 113.9	~0	—
2		121.7, 115.4	~0	—
3		122.1, 115.3	16	(*R*)
4		127.4, 124.5	25	(*R*)
5		110.6, 108.8	39	(*R*)
6		116.9, 113.7	17	(*S*)
7		112.5, 110.5	41	(*S*)
8		114.0, 111.4	55	(*S*)
9	Et	146.8, 143.9	18	(*R*)
10	Cy	151.9, 148.1	59	(*R*)

[a] Ar of 4 was phenyl except entry 1 in which 2-naphthyl was applied. [b] Chemical shifts of the ligands in $CDCl_3$. 85% H_3PO_4 was a reference standard. [c] Determined by HPLC analysis with a chiral column (Daicel OJ). [d] Determined by the major peak of HPLC analysis from an authentic (*R*) major sample by the reaction with (*S,S*)-CHIRAPHOS.



AGAIN, SYSTEM IS UNDERDEFINED FROM THESE EXPERIMENTS.

RAJANBABU, T.V.; et al SYNLETT (1996) 745.

CONCLUSIONS.

- FLUORINE SUBSTITUTION CLEARLY AFFECTS REACTIVITY AND SELECTIVITY.
- A NUMBER OF INTERACTIONS HAVE BEEN IDENTIFIED WHICH CAN ONLY BE RATIONALIZIED IN TERMS OF C-F-M INTERACTIONS.
- SOME HAVE CLEARLY BE MIS-INTERPRETED, AS:
  - SOME KIND OF STERIC OR STERED ELECTRONIC EFFECT
  - SOMETHING STRANGE
- SYSTEMATIC ANALYSIS (POSS. ^{19}F NMR) NEEDS TO BE USED TO BETTER UNDERSTAND THESE INTERACTIONS.

THE END

OTHER REFERENCES OF NOTE

TOGNI, A; HINTERMANN, L. ACIEE (2000) 39 4359.

MURRAY-RUST, P., et al J. AM. CHEM. SOC (1983) 105 3206.

SEEBACH, D; ACIEE (1990) 29 1325.

ISERI, K. J. SYNTH ORG. CHEM JPN. (2000), 119.

DUTHALER, R.O. ACIEE (1997) 36, 43.

RICHMOND, T.G. ACIEE (1999) 39, 3241.