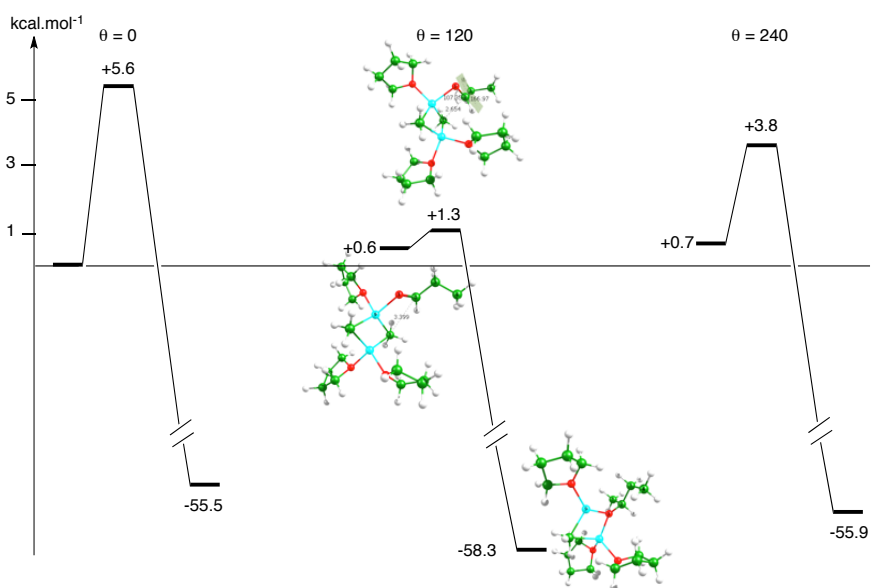# Base or Nucleophile? DFT Finally Elucidates the Origin of the Selectivity Between the Competitive Reactions Triggered by MeLi or LDA on Propanal
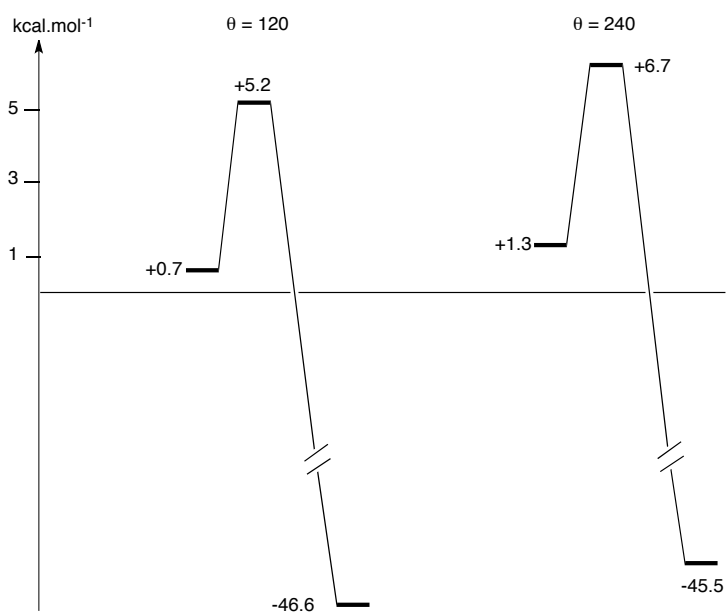
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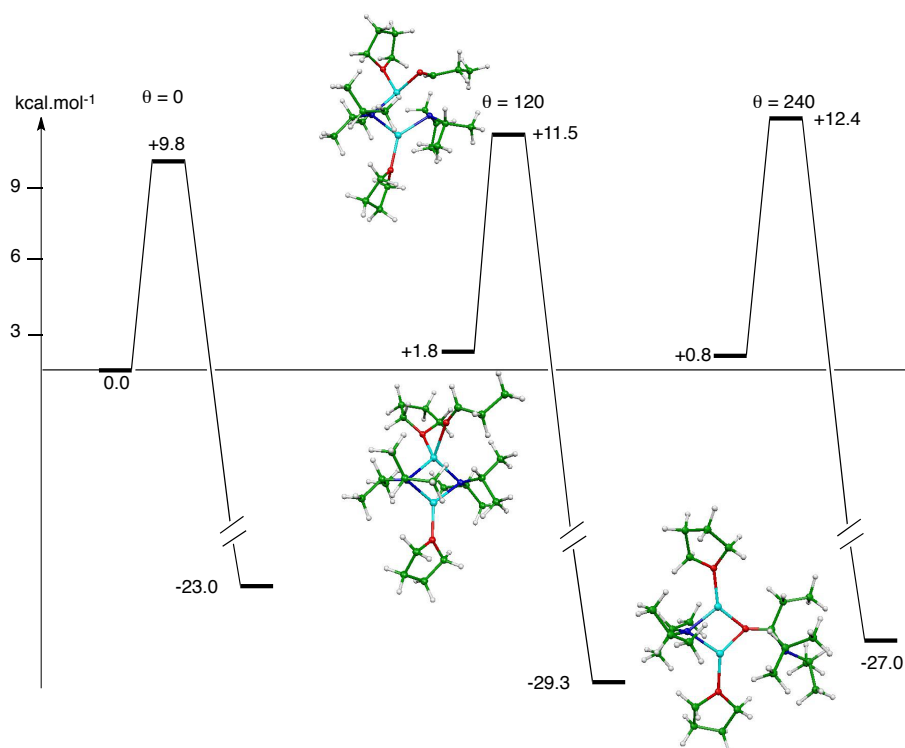
Supplementary Information

Figure 1S : Energy profiles for the addition ($\gamma = 0$) of the three conformers of propanal ($\theta = 0, 120, 240$) by $(MeLi)_2$-3THF.

Figure 2S : Energy profiles for the deprotonation ($\gamma = 180$) of two conformers of propanal ($\theta = 120, 240$) by $(MeLi)_2$-3THF.

Figure 3S : Energy profiles for the addition ($\gamma = 0$) of the three conformers of propanal ($\theta = 0, 120, 240$) by $(LDA)_2$-2THF.

Table 1S. Geometrical characteristics of the deprotonation pathway ($\gamma = 180$).[a]

Entry	Geom.[b]	Status[c]	$(MeLi)_2$	$(LDA)_2{}^{240}$	$(LDA)_2{}^{120}$
1	C^2-H	Cpx	1.097	1.093	1.093
		TS	1.292	1.273	1.307
2	X-H^a	Cpx	2.579	4.355	4.143
		TS	1.620	1.625	1.507
3	Li^A-O-C^1	Cpx	121.2	161.3	161.4
		TS	113.4	112.3	100.1
4	Li^A-O-C^1-C^2	Cpx	4.4	2.2	5.8
		TS	-25.4	20.5	-69.2
5	X-Li^A-O-C^1	Cpx	-59.4	86.8	-43.2
		TS	-33.1	35.8	53.4
6	H^2-C^2-C^1-O	Cpx	22.37	-7.570	9.315
		TS	59.56	-63.05	54.84

[a] $(LDA)_2{}^{240}$ and $(LDA)_2{}^{120}$ stand for $\theta = 240$ and 120, respectively; [b] distances (2 first entries) are in Å and angles (3 last entries) in degrees; b Cpx = starting complex.