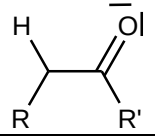
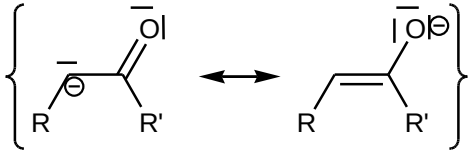
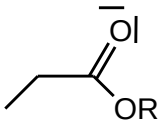
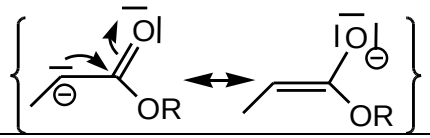
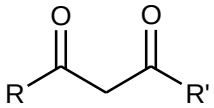
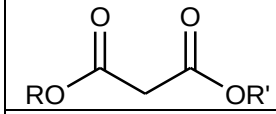
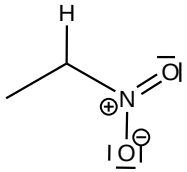
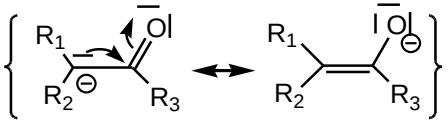
pKa des couples dont la base carbanion est stabilisée

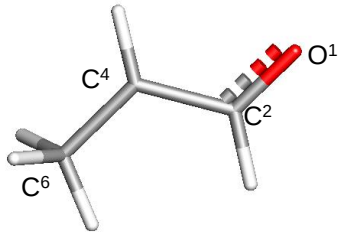
Acide	Base	pKa
Cétone/ Aldéhyde 		≈20
ester 		≈25
Chlorure d'acyle		≈16
Amide tertiaire		≈30
β-dicétones 		≈9
β-diester 		≈13
Nitroalcanes 		≈10

Structure électronique de l'énolate

Par mésomérie

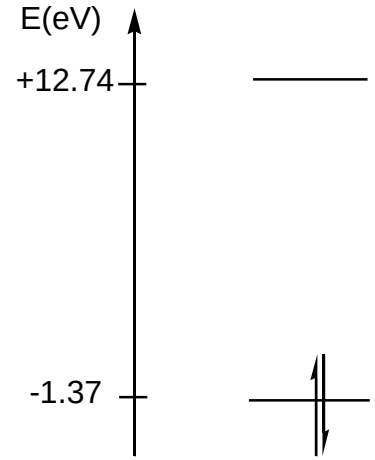


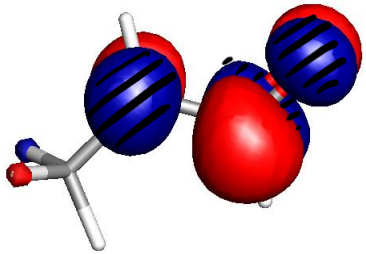
prépondérante

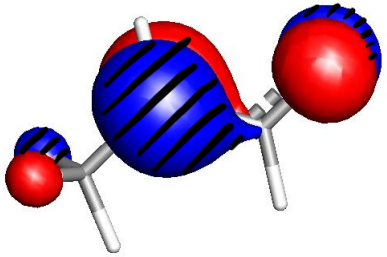


⇒ caractère **très** Nucléophile de ……

Par les OF







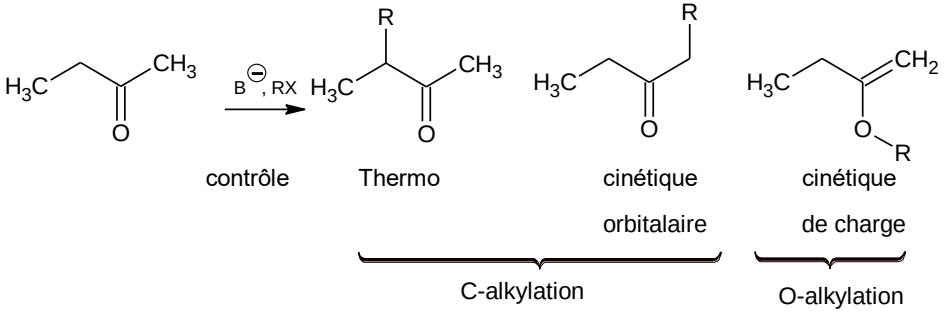
<u>Sous contrôle orbitalaire</u>, le site le plus nucléophile est :

Charges de Mulliken

1 O	2 C	3 H	4 C	5 H	6 C	7 H	8 H	9 H
-0.697	0.441	-0.143	-0.561	0.032	0.066	-0.039	-0.049	-0.049

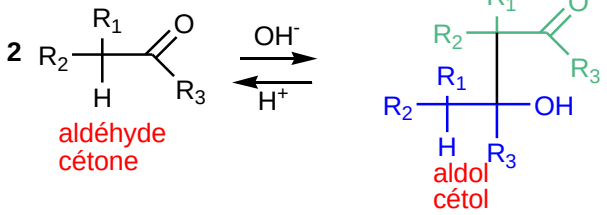
<u>Sous contrôle de charge</u>, le site le plus nucléophile est :

Contrôle cinétique – Contrôle thermodynamique : régiosélectivité



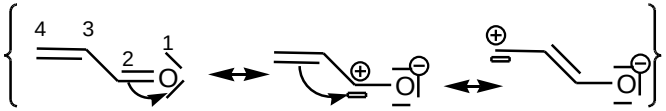
Contrôle	Thermodynamique	Cinétique orbitalaire	Cinétique de charge
Base	Peu encombrée H^-	Très encombrée : LDA	
T	haute	basse	
t	long	court	
RX		$H_3C—I$ (δ+ δ-)	$H_3C—O—S(=O)_2—O—CH_3$ (δ+ δ- δ- δ+)
Solvant		Polaire/ Non dissociant : Ether/THF	Polaire / dissociant : DMSO

Aldolisation / cétolisation



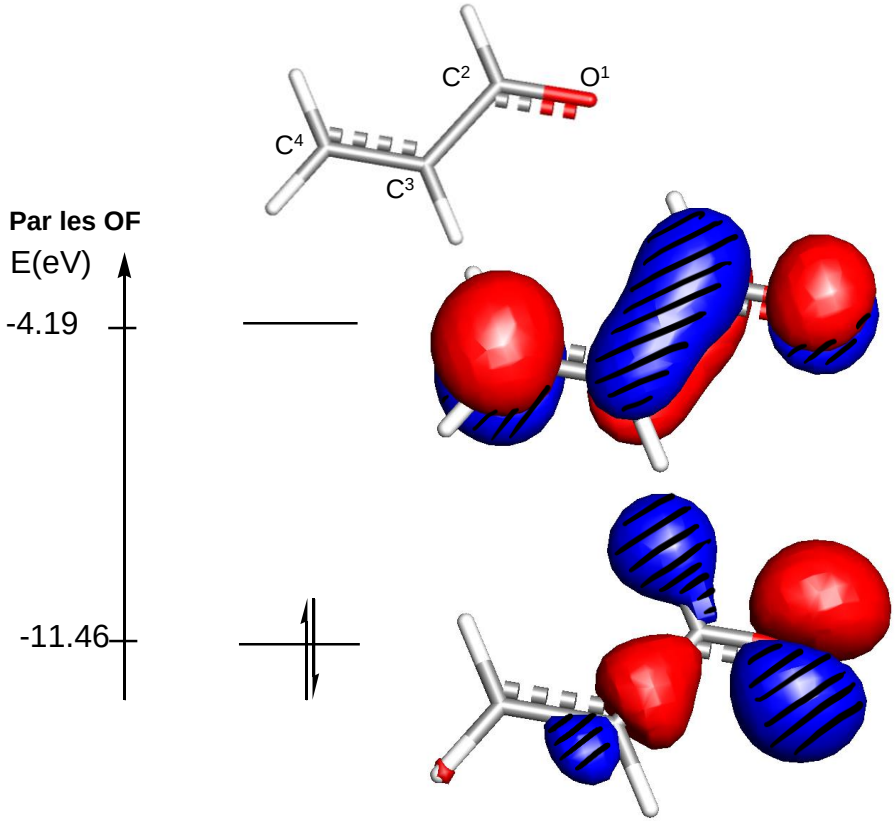
Structure électronique des α-énones : Par la théorie des OF

Par mésomérie



⇒ caractère **très** électrophile de ……

Par les OF



Sous contrôle orbitalaire, le site le plus électrophile est :

Décomposition en CLOA des OM 9 à 13 de l'acroléine, axe z perpendiculaire à la molécule.

		9-( )	10-( )	11-( )	12-( )	13-( )
ENERGY =		-16.8816	-15.5204	-11.4571	-4.1946	6.0040
1 O	2 s	0.36649	0.00000	0.00022	0.00000	0.00000
1 O	2 px	0.67268	0.00000	0.51934	0.00000	0.00000
1 O	2 py	-0.47838	0.00000	0.79571	0.00000	0.00000
1 O	2 pz	0.00000	0.59530	0.00000	0.60700	0.44655
2 C	2 s	-0.05109	0.00000	0.02879	0.00000	0.00000
2 C	2 px	-0.28998	0.00000	-0.11710	0.00000	0.00000
2 C	2 py	0.11895	0.00000	-0.10178	0.00000	0.00000
2 C	2 pz	0.00000	0.24701	0.00000	-0.54715	-0.80342
3 C	2 s	0.03243	0.00000	0.12243	0.00000	0.00000
3 C	2 px	0.20633	0.00000	0.27896	0.00000	0.00000
3 C	2 py	0.03801	0.00000	0.12707	0.00000	0.00000
3 C	2 pz	0.00000	-0.42649	0.00000	-0.43235	0.85275
4 C	2 s	-0.03627	0.00000	-0.02426	0.00000	0.00000
4 C	2 px	-0.12244	0.00000	-0.07863	0.00000	0.00000
4 C	2 py	-0.01754	0.00000	0.01111	0.00000	0.00000
4 C	2 pz	0.00000	-0.52527	0.00000	0.72555	-0.52577

Charges de Mulliken

1 O	2 C	3 C	4 C	5 H	6 H	7 H	8 H
-0.392	0.454	-0.087	0.027	-0.076	0.040	0.016	0.017

Sous contrôle de charge, le site le plus électrophile est :