Carbonyl and Related Compounds

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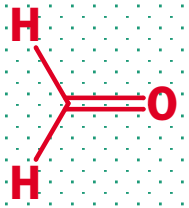
Addition to C=O: structure, reactivity and preparation of carbonyl compounds; mechanism (with evidence), reactivity, equilibrium and kinetic control; formation of hydrates, cyanohydrins and bisulphite adduct; nucleophilic addition-elimination reactions with alcohols, thiols and nitrogen- based nucleophiles;

reactions: benzoin condensation, Cannizzaro and Tischenko reactions, reactions with ylides: Wittig and Corey-Chaykovsky reaction; Rupe rearrangement, oxidations and reductions: Clemmensen, Wolff-Kishner, $LiAlH_4$, $NaBH_4$, MPV, Oppenauer, Bouveault-Blanc, acyloin condensation; oxidation of alcohols with PDC and PCC; periodic acid and lead tetraacetate oxidation of 1,2-diols.

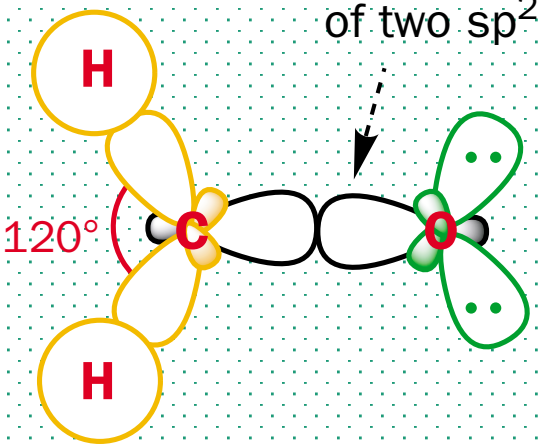
MO Structure of carbonyl



formaldehyde

σ bonding in formaldehyde

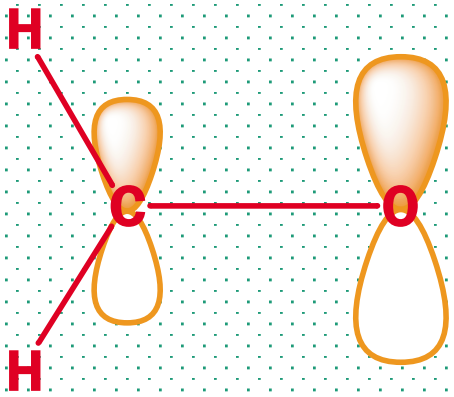
C–O σ bond made up of two sp^2 orbitals



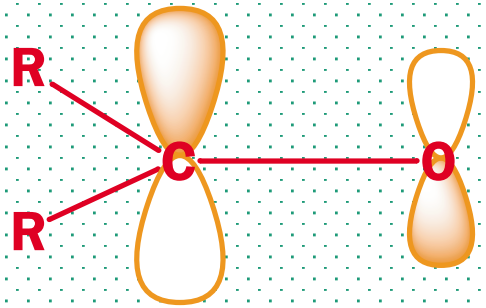
remaining sp^2 orbitals on C form bonds to H

remaining sp^2 orbitals on O contain lone pairs

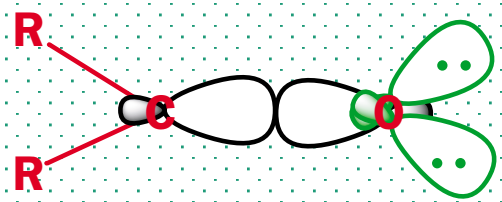
π bonding in formaldehyde



C–O π bond made up of two p orbitals

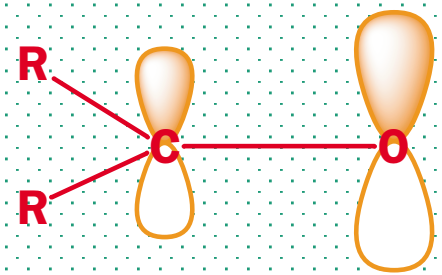


empty, antibonding π^* orbital



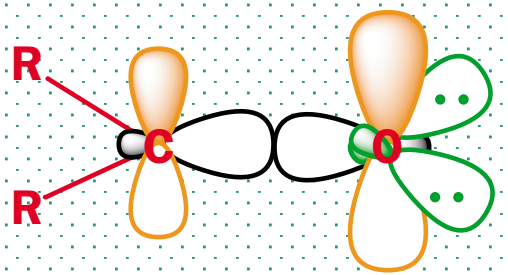
filled σ sp^2 (lone pair) orbitals

+



filled π orbital

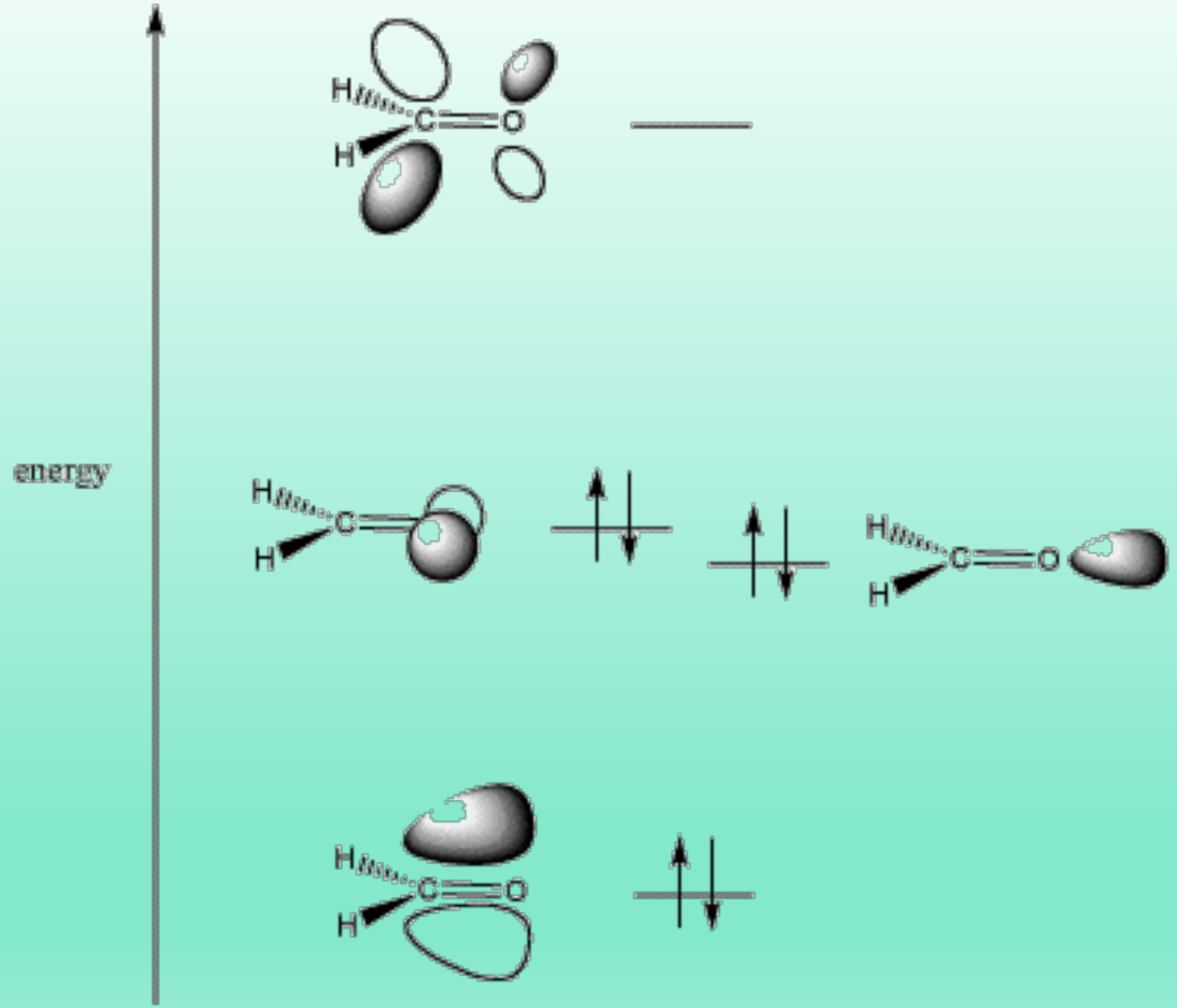
=



complete diagram of filled orbitals of C=O bond

Electronegativities, bond lengths, and bond strengths

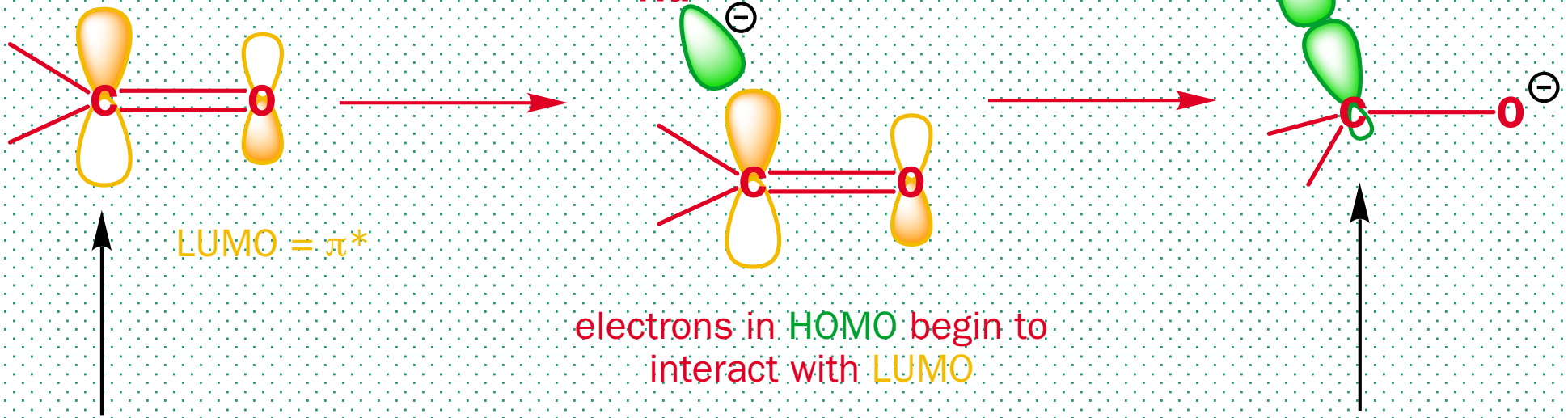
Representative bond energies, kJ mol^{-1}				Representative bond lengths, Å				Electronegativity			
C–O	351	C=O	720	C–O	1.43	C=O	1.21	C	2.5	O	3.5



Frontier orbitals in a carbonyl compound

Nucleophilic Addition Reaction to carbonyl

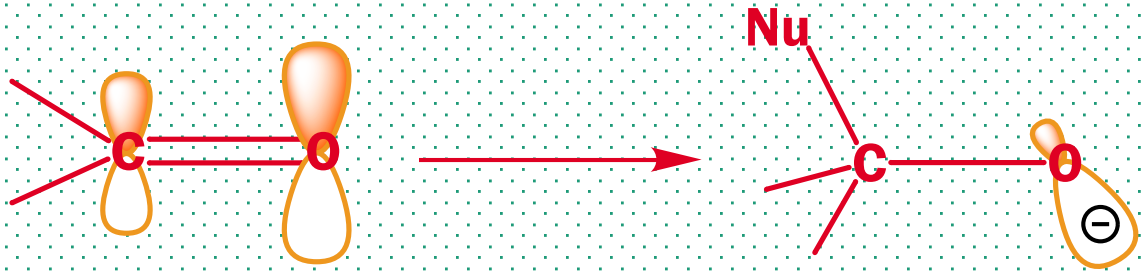
orbitals involved:



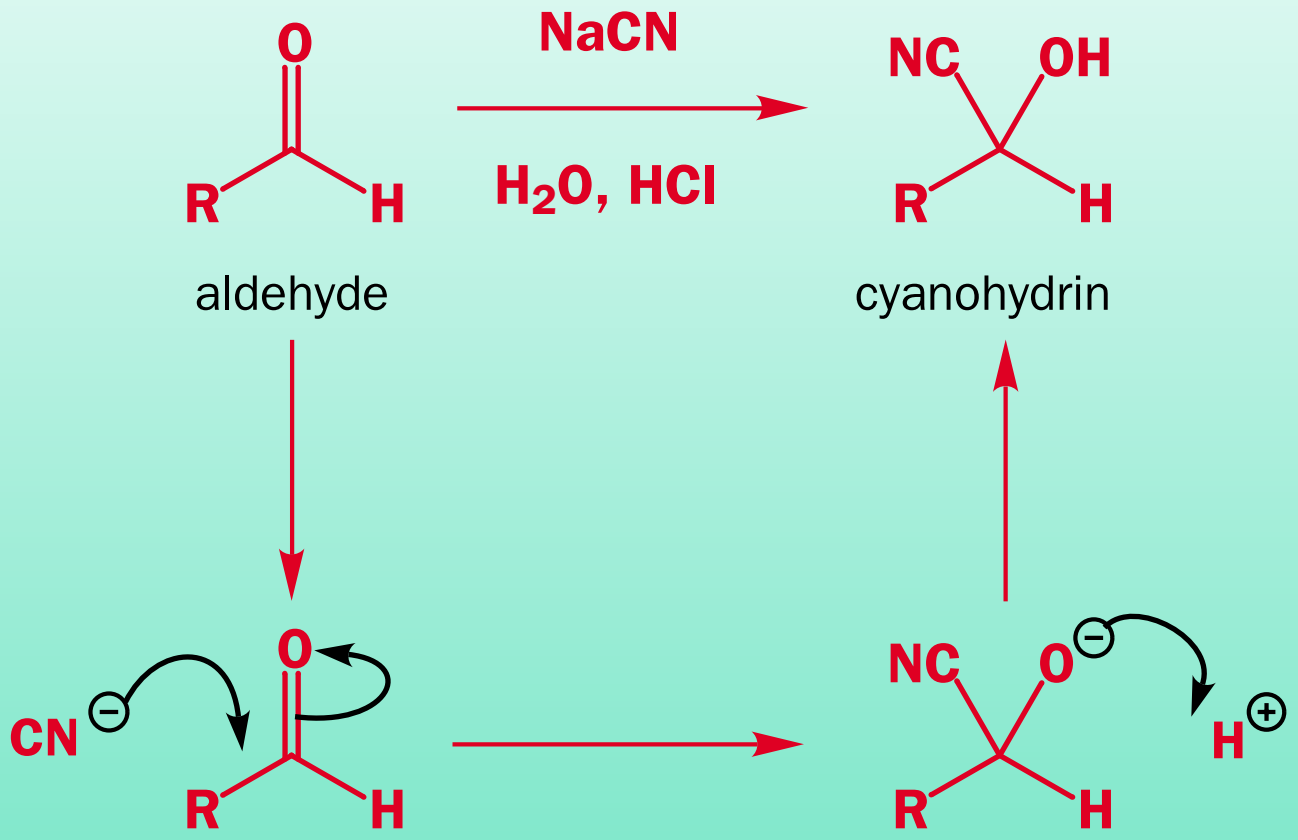
sp^2 hybridized carbon

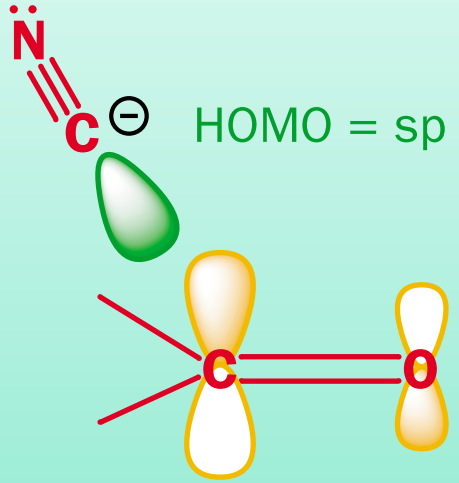
sp^3 hybridized carbon

while at the same time...



Nucleophilic Addition Reaction to carbonyl





HOMO = sp orbital

LUMO = π*

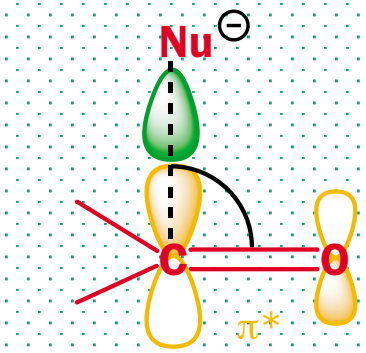
orbitals involved in the addition of cyanide

The angle of nucleophilic attack

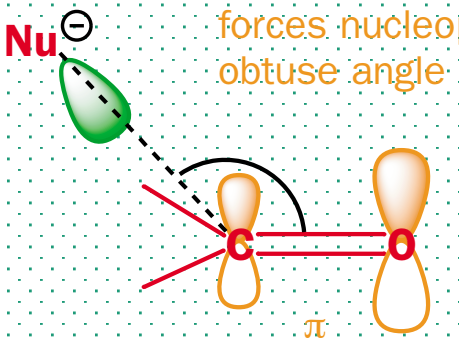
The Bürgi–Dunitz angle trajectory

Nucleophiles attack not from a direction perpendicular to the plane of the carbonyl group but at about 107° to the C=O bond.

This approach route is known as the Bürgi–Dunitz trajectory.



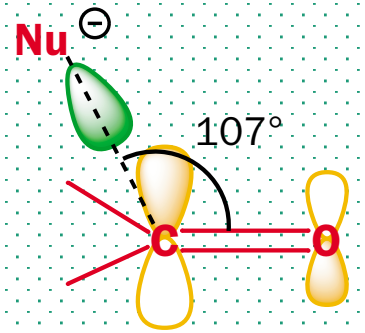
maximum overlap with π*
perpendicular to C=O bond



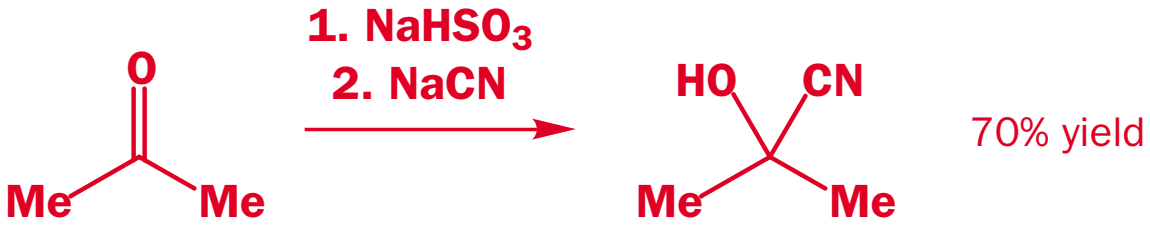
repulsion from filled π orbital
forces nucleophile to attack at
obtuse angle

combined effect:

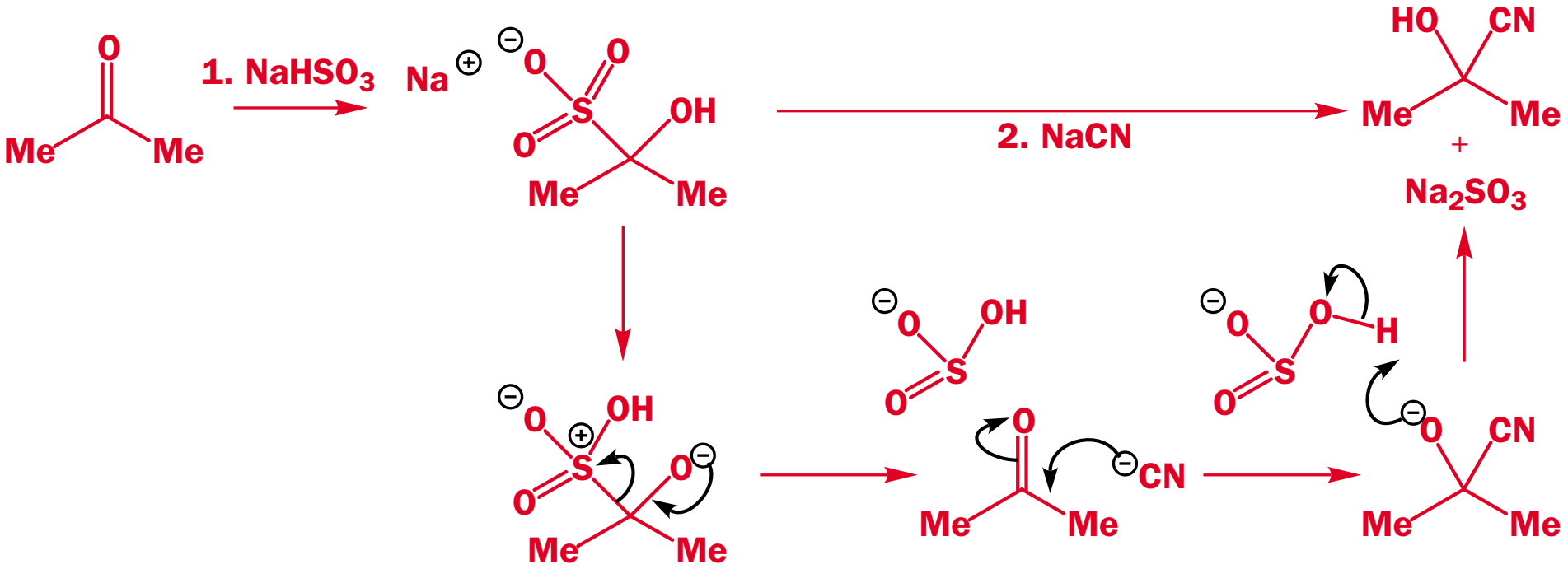
nucleophile attacks
C=O at 107° angle



Cyanohydrin reaction

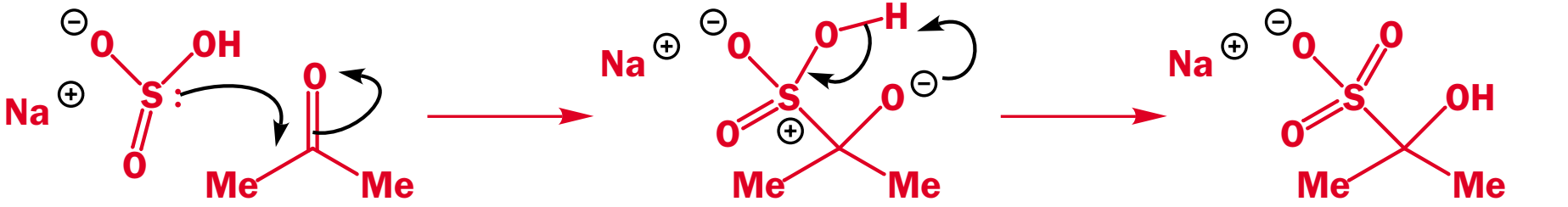


70% yield

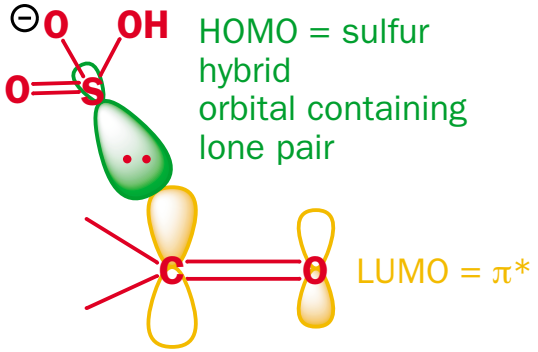


Bisulfite addition compounds

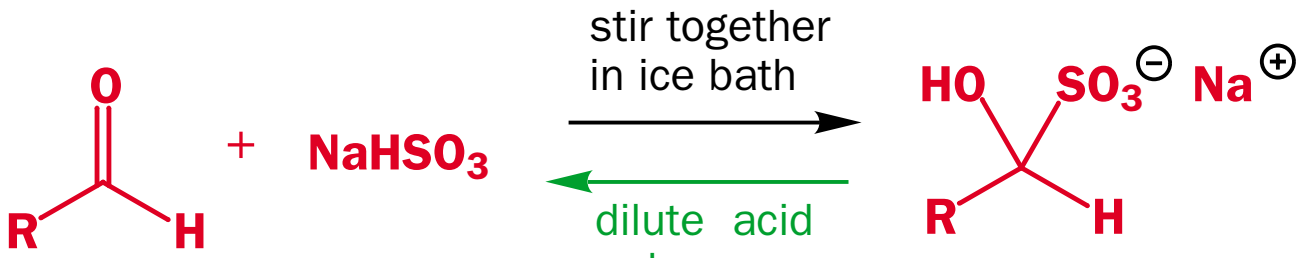
sodium bisulfite



bisulfite addition compound

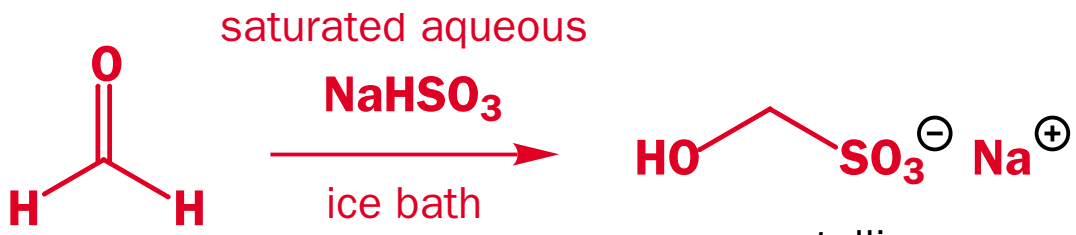


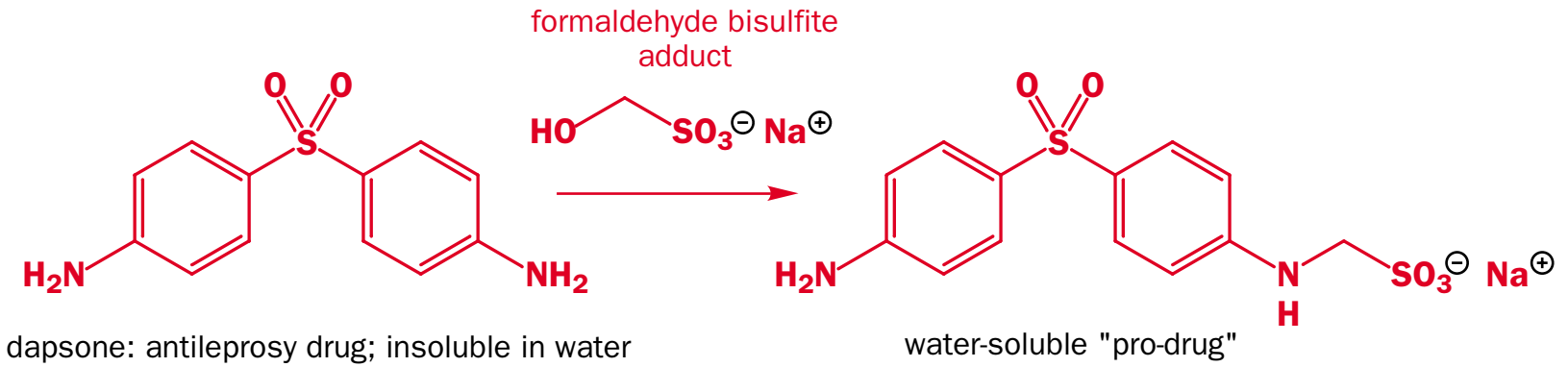
orbitals involved in the addition of bisulfite



crystalline solid

Bisulfite Addition Reaction

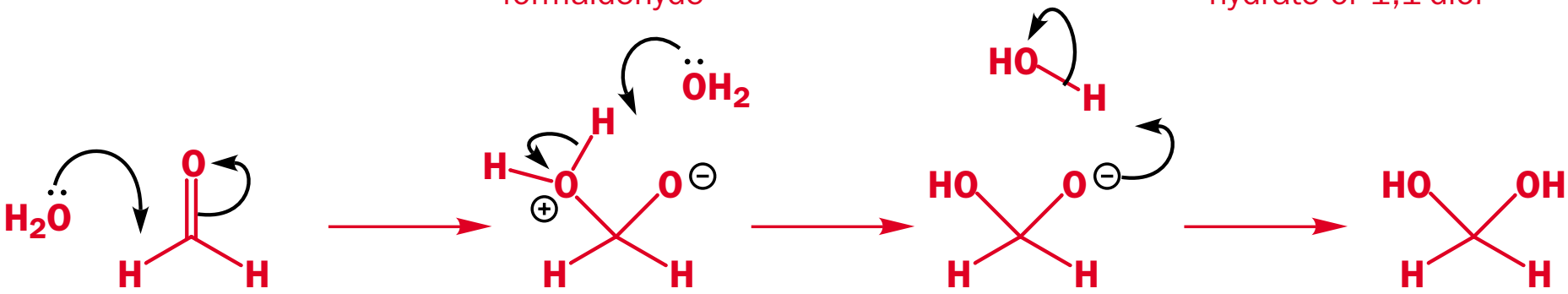


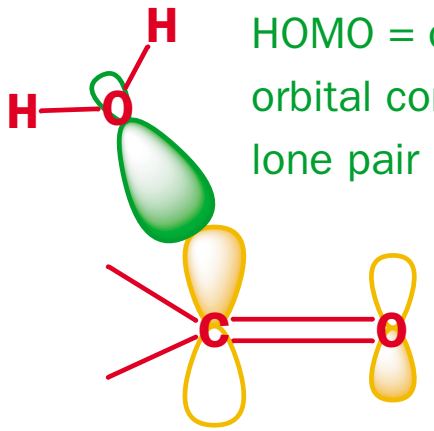


Formation of hydrates of carbonyl Compounds

formaldehyde

hydrate or 1,1-diol



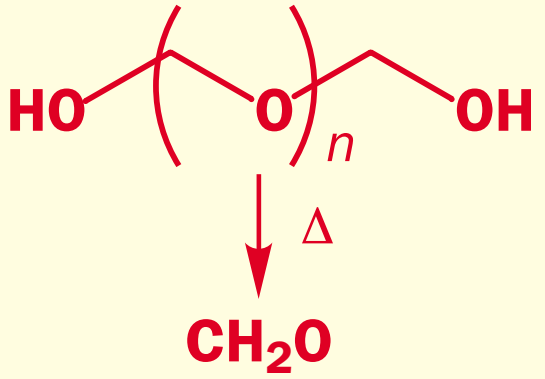


HOMO = oxygen sp^3 orbital containing lone pair

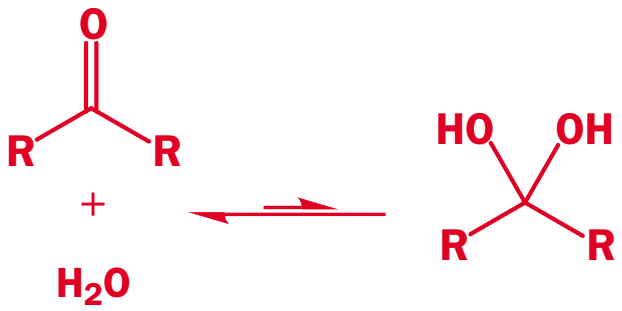
LUMO = π^*

orbitals involved in the addition of water

polymeric ‘paraformaldehyde’

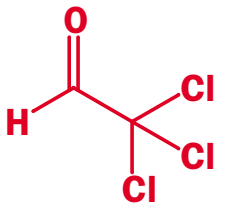
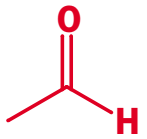
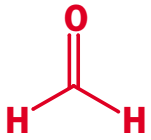
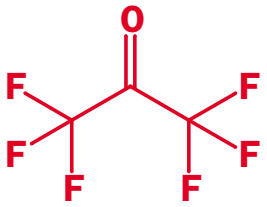


Rate of Hydration Reaction of carbonyl compounds



significant concentrations of hydrate are generally formed only from aldehydes

equilibrium constant *K*

acetone		0.001	chloral		2000
acetaldehyde		1.06			
formaldehyde		2280	hexafluoroacetone		1 200 000

Cyclopropanone easily undergoes hydration