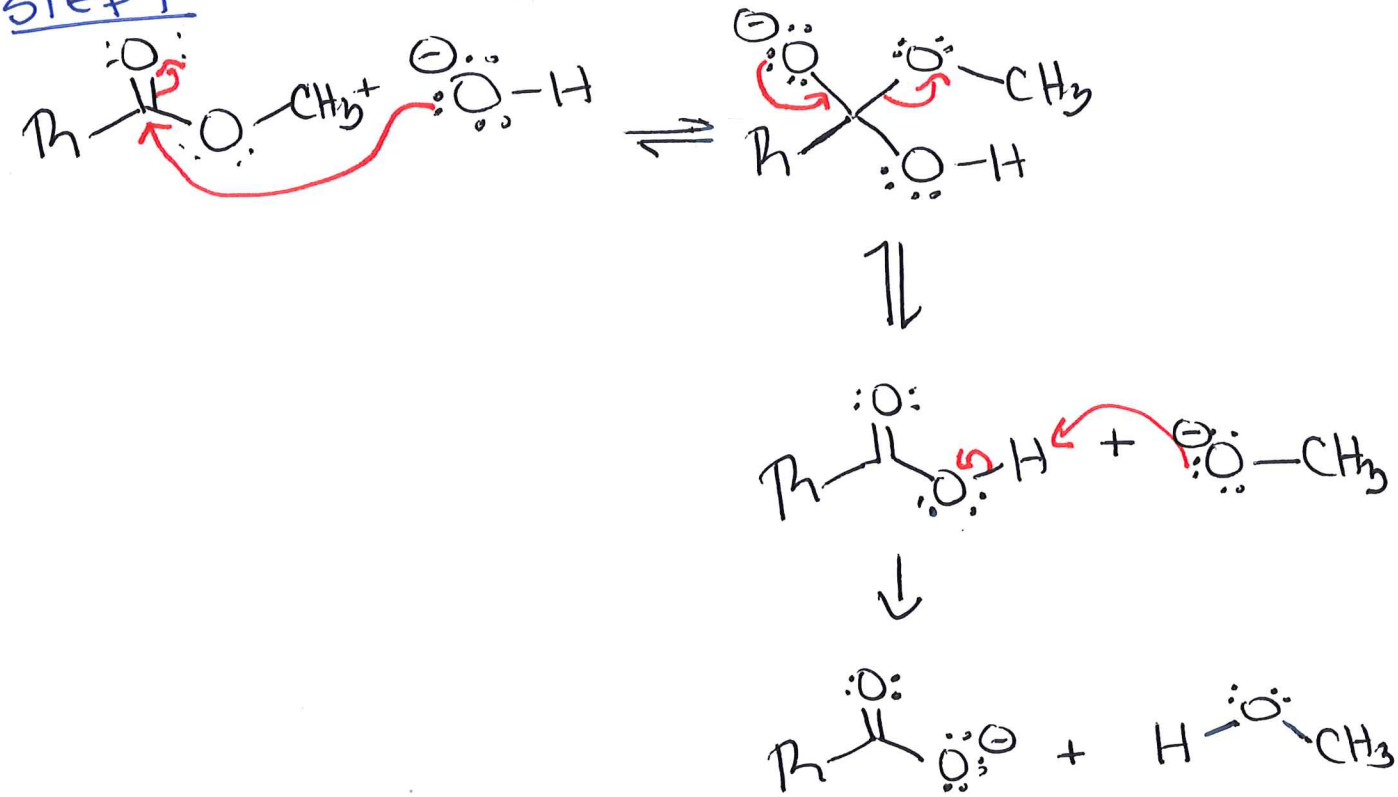
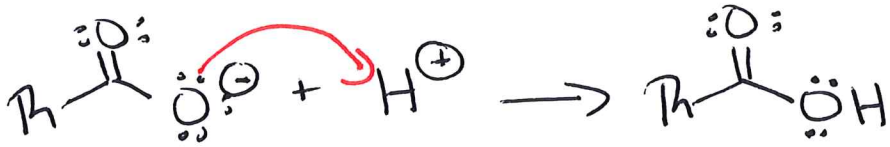
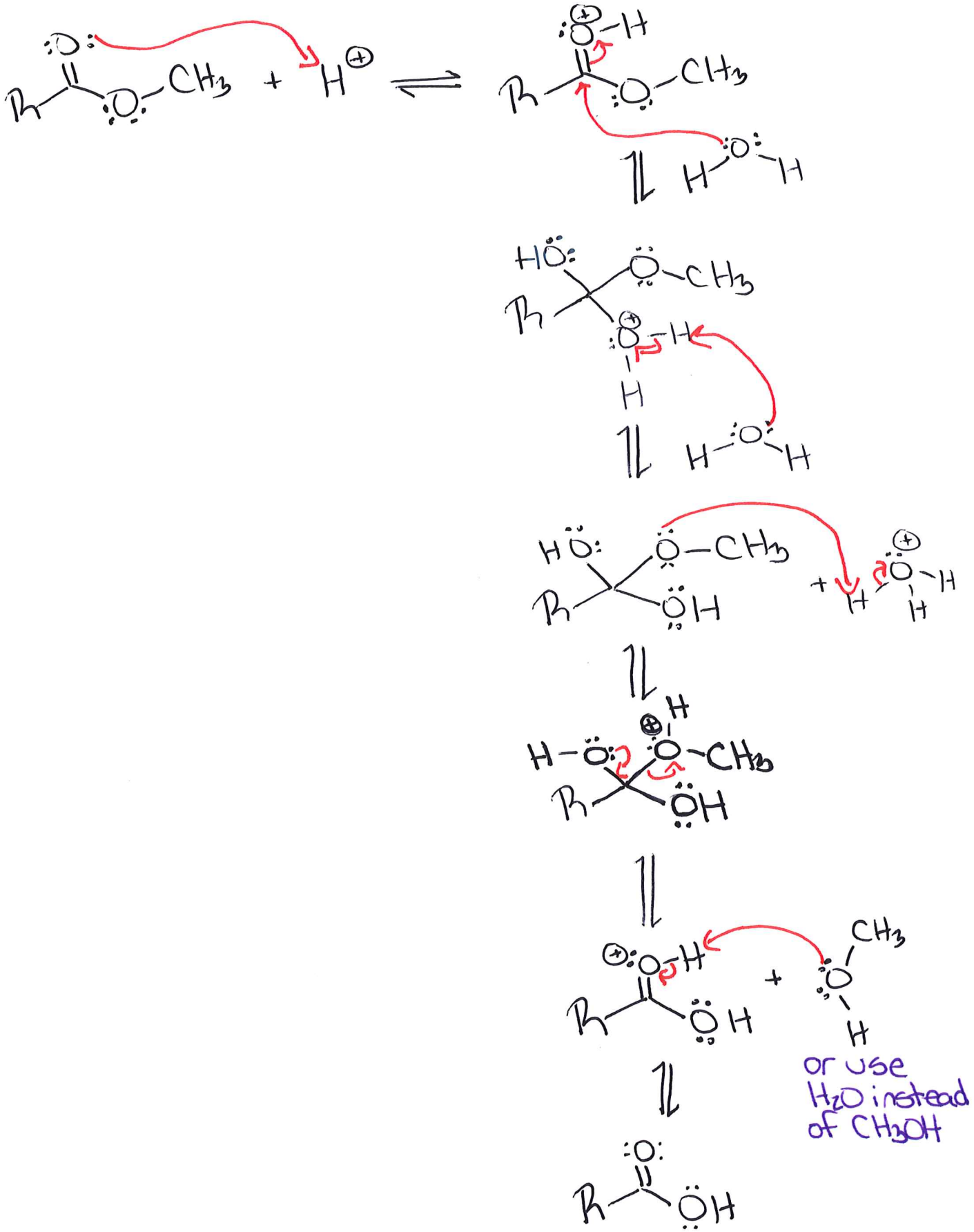
1. (a) STEP 1



STEP 2



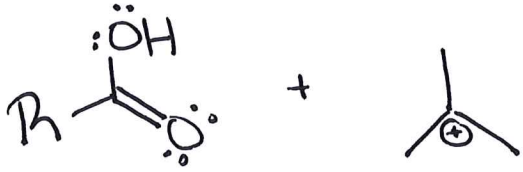
1. (b)



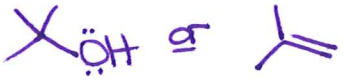
or use H_2O instead of CH_3OH

1. (c)

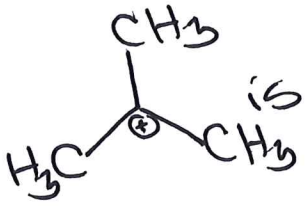
resonance-stabilized cation (∴ better than protonating other O)



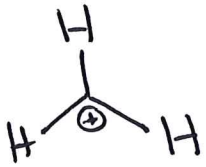
reacts w/ H_2O to give either



(d)



is a tertiary carbocation

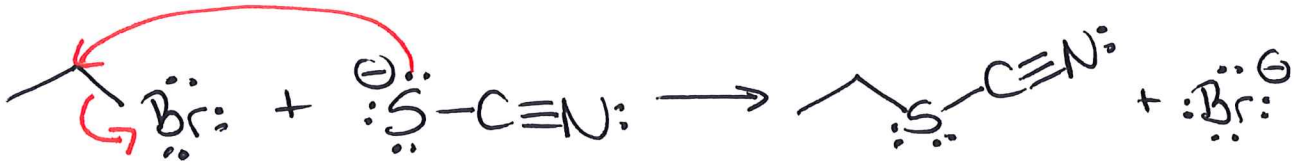


is a primary carbocation.

Due to inductive effects (alkyl groups are electron-donating), tertiary carbocations are much more stable than primary carbocations. The second step of the mechanism could not occur if the carbocation were primary.

2. (a) 

(b) 

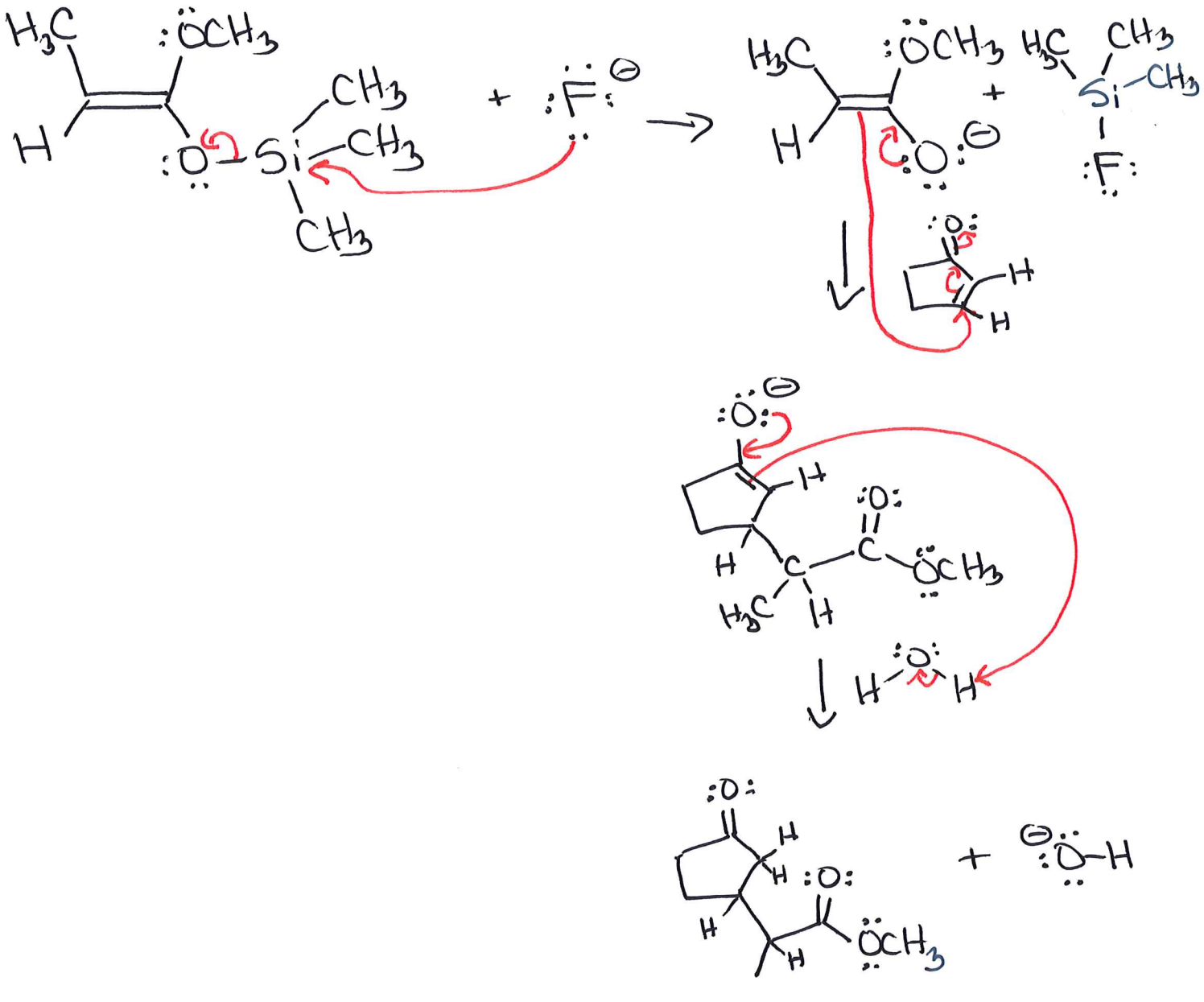
(c) 

(d)  is a soft electrophile. The electronegativity of Br is only slightly higher than that of C, so the charge density ($\delta+$) on C is low.

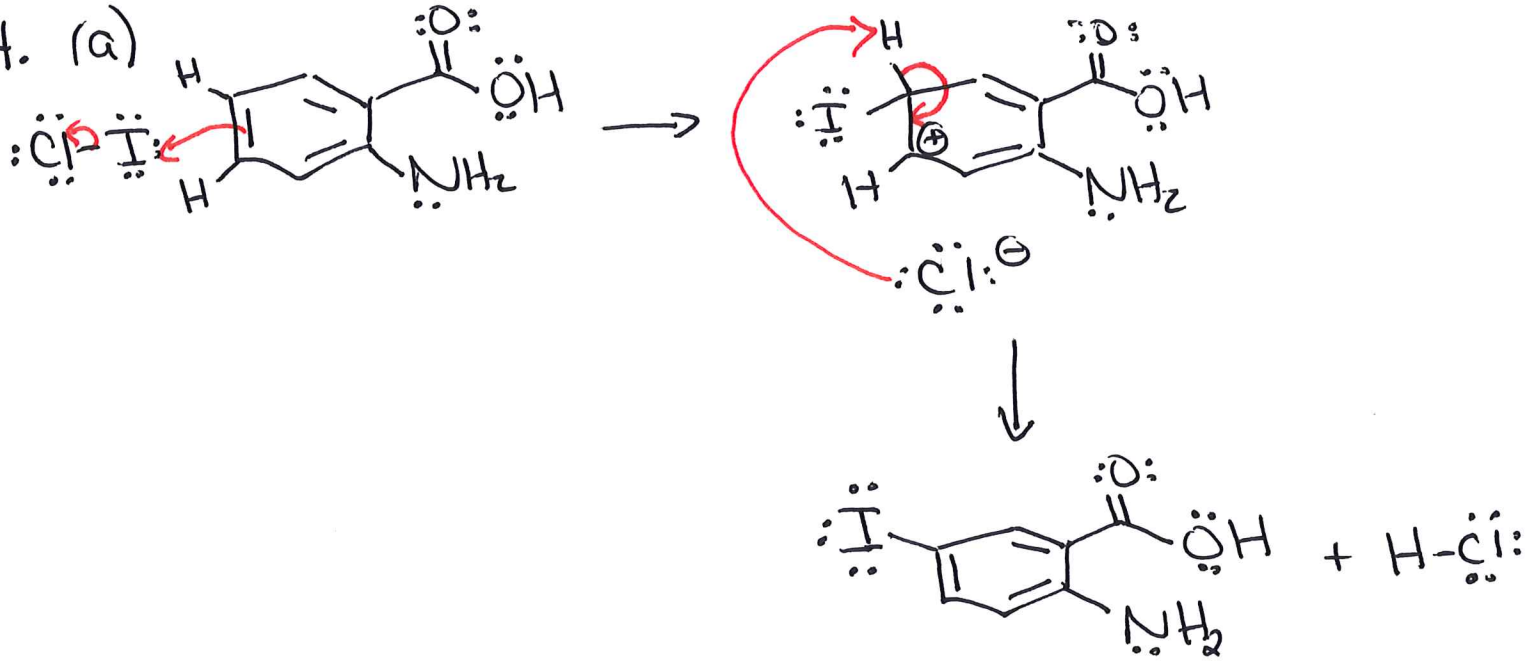
In the thiocyanate ion, S is the softer nucleophilic site and N is the harder nucleophilic site. S is much larger than N so, even though both atoms have a charge of about $-\frac{1}{2}$, the charge density of S is lower.

Soft electrophiles tend to react with softer nucleophiles, so we expect formation of a C-S bond (not a C-N bond).

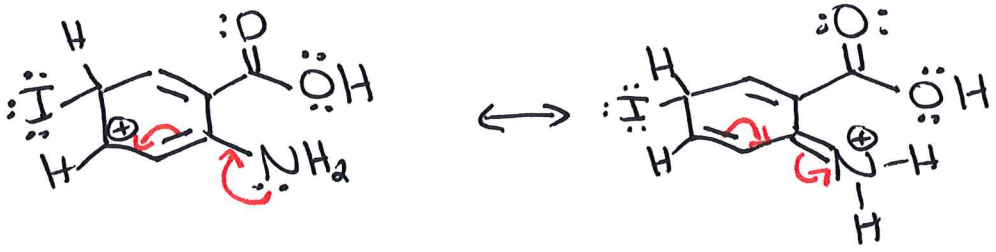
3.



4. (a)



(b) In the absence of acid (ie when it is not protonated to $-\overset{\oplus}{N}H_3$), the $-\ddot{N}H_2$ group is an electron donating group. As such, it activates the benzene ring (making it more nucleophilic) and is an ortho/para director. It provides additional resonance-stabilization to the carbocation intermediates involved in ortho or para substitution:



The para site is more accessible than the ortho site, so sterics favor the observed product.

While the carboxylic acid group is a meta director, favoring the same products, the effect(s) of activating group(s) dominate over deactivating groups.