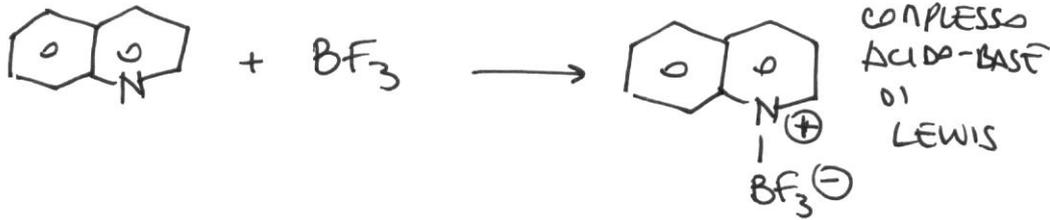


# REATIVITA' DELLA CHINOLINA

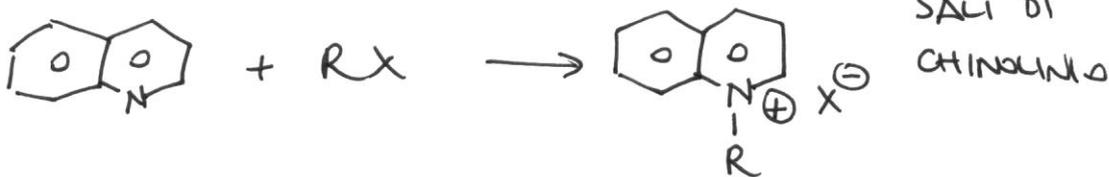
(3)

## ① Reazioni su N:

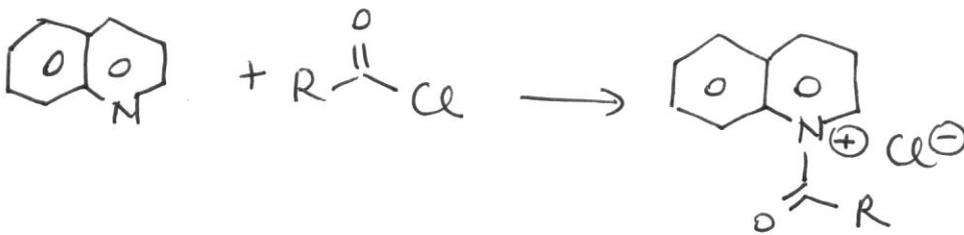
### Ⓐ CON ACIDI DI LEWIS:



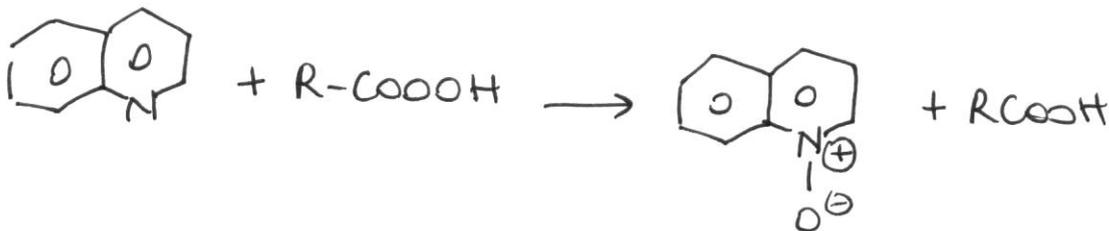
### Ⓑ ALCHILAZIONE:



### Ⓒ ACILAZIONE:

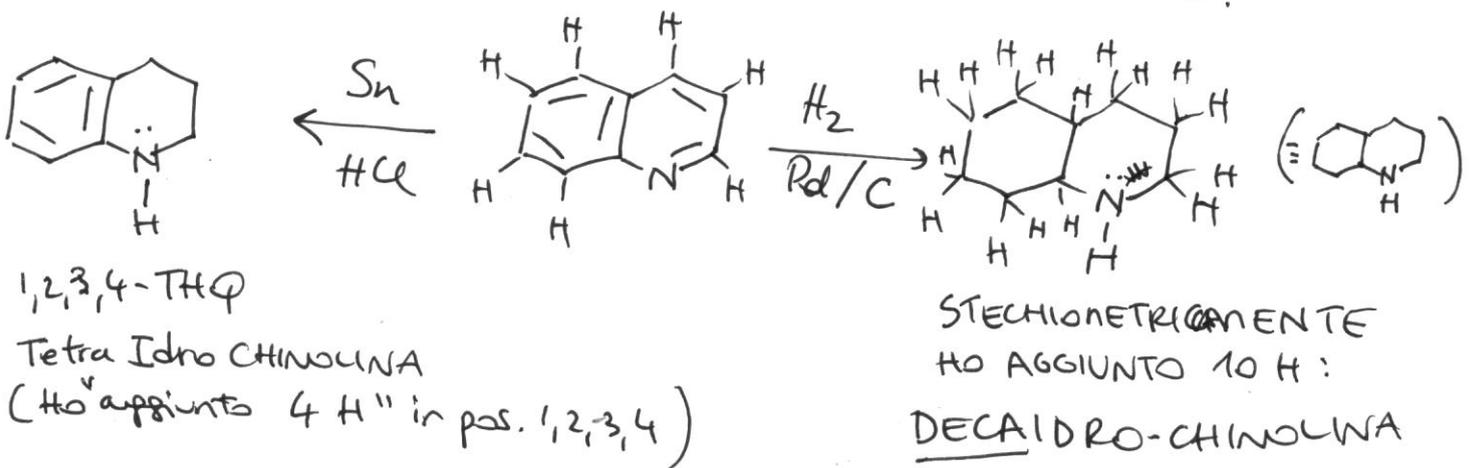


### Ⓓ FORMAZIONE DI N-OSSIDI CON PERACIDI



SIMILE ALLA PIRIDINA

NB: questa è una OSSIDAZIONE. E la RIDUZIONE?

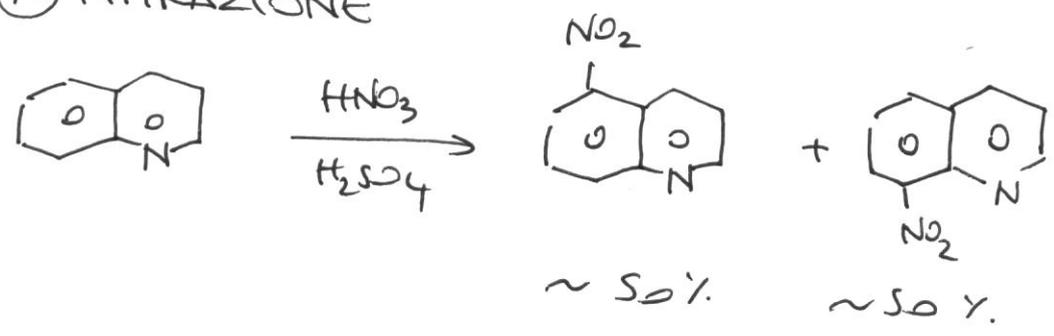


# ② SOSTITUZIONI ELETTROFILI AROMATICHE

\* preferenzialmente su anello "benzenico" perché l'altro è impoverito sui C dalle strutt. ris. che portano densità e<sup>-</sup> su N.

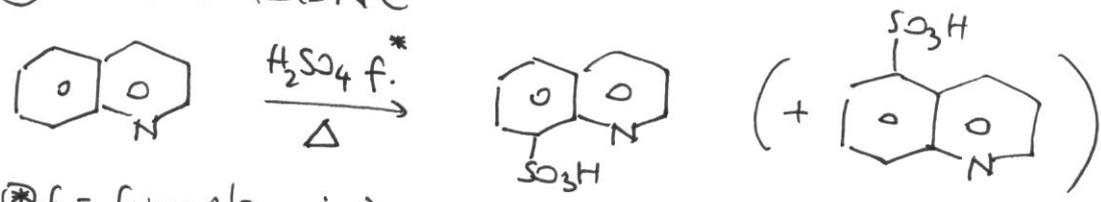
\* IN CONDIZIONI ACIDE si protona "N", che viene disattivato e le sostituzioni avvengono preferenzialmente in C-5 e C-8

## (A) NITRAZIONE



pH molto ACID

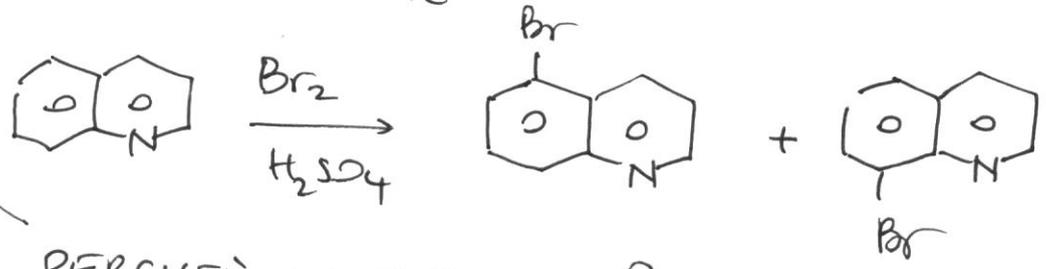
## (B) SOLFONAZIONE



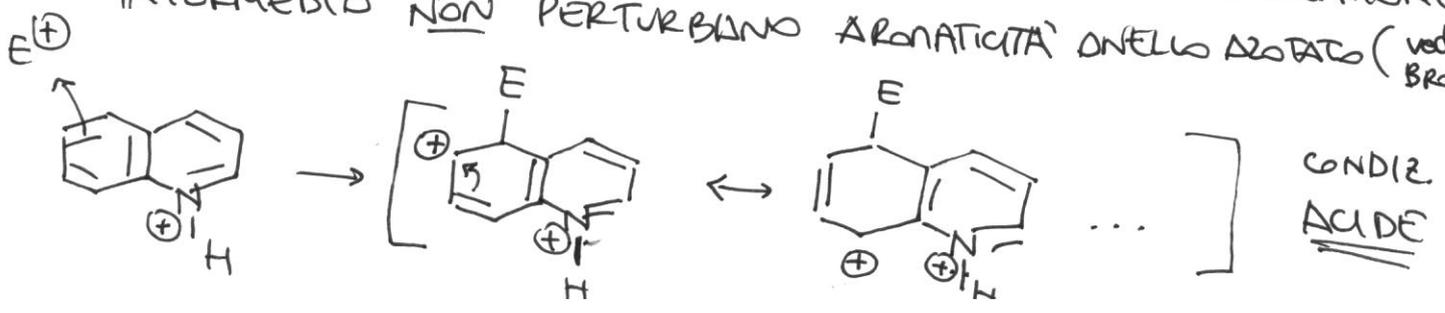
proporzioni tra prodotti dipende da condizioni (T, t, ...)

\* f = fumante, cioè con 30% SO<sub>3</sub>

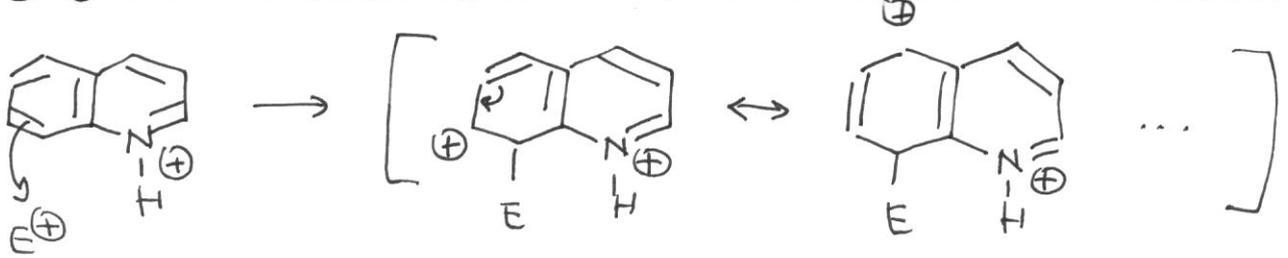
## (C) ALOGENAZIONE



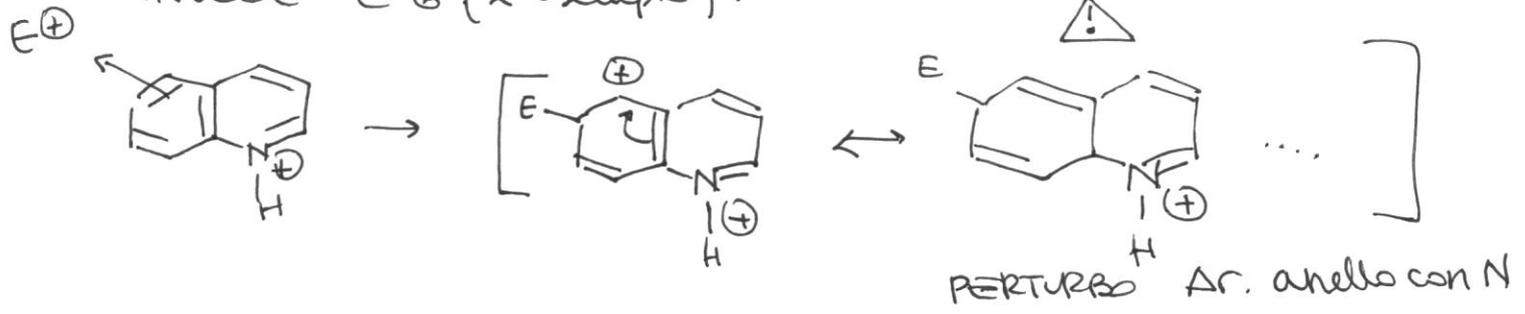
PERCHE' IN C-5 e C-8? PERCHE' STRUTT. RIS. CARBOCATIONE INTERMEDIO NON PERTURBANO AROMATICITA' NELL'AZOTATO (vedi BROWN)



C-6:



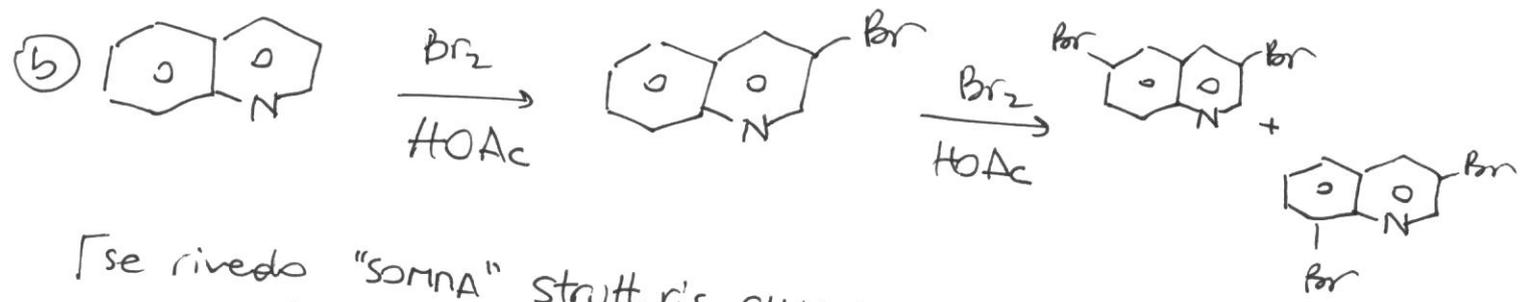
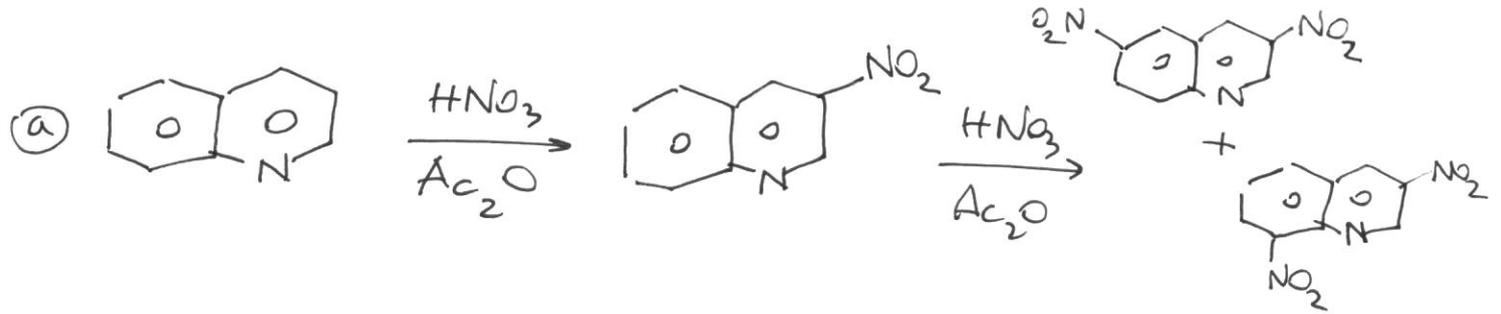
INVECE C-6 (x esempio):



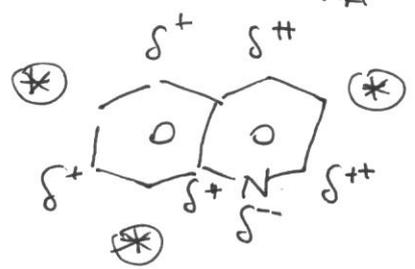
simile per C-7...

ATTENZIONE, SE USO CONDIZIONI POCO ACIDE (ACIDI ORGANICI anziché INORGANICI OPPURE  $Ac_2O$  PER MITIGARE  $HNO_3$ ) ALLORA SE AR PREFERENZIALE:

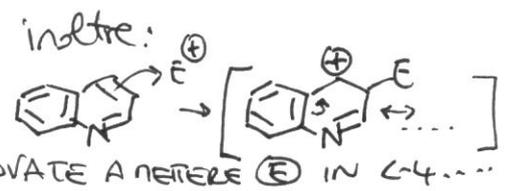
- IN C(3)
- A SEGUIRE C(6) e C(8)



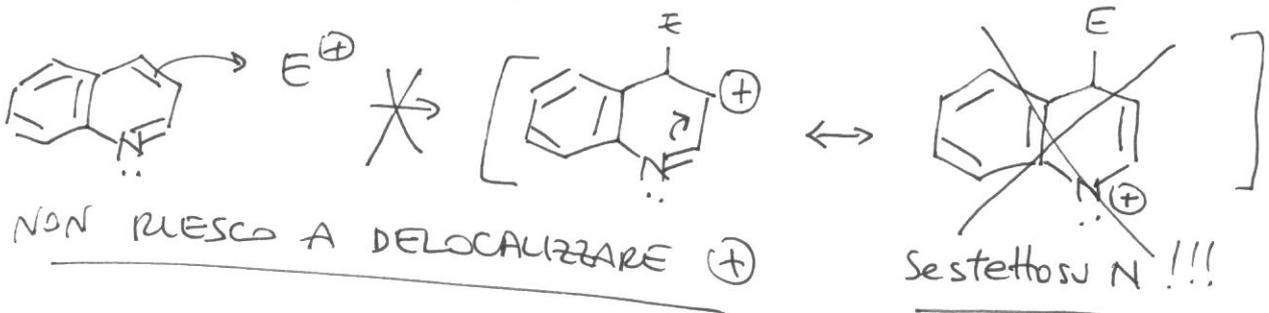
Se rivedo "SOMMA" strutt. ris. CHANOLINA:



C-3 } meno preferibile  
 C-6 } di e- non  
 C-8 } hanno carica (+)  
 in strutt. ris.  
 CHANOLINA



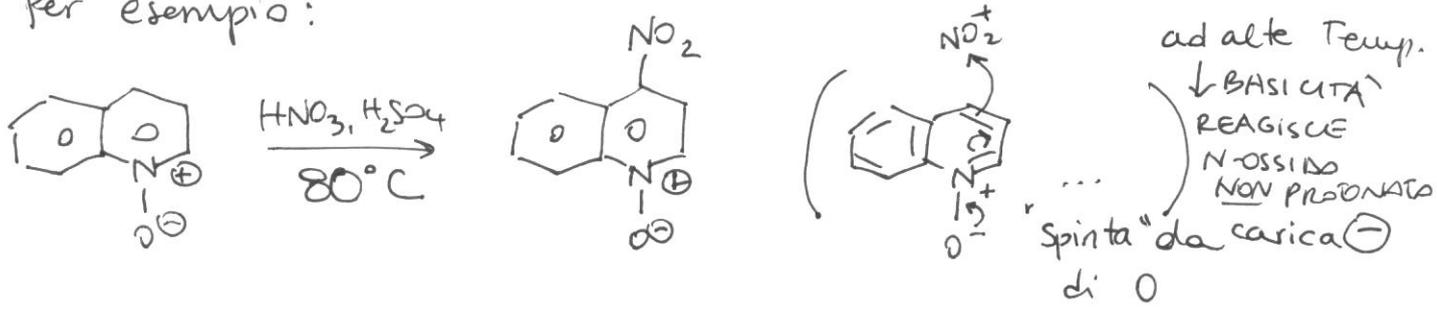
Se provo a mettere (E) in C-4:



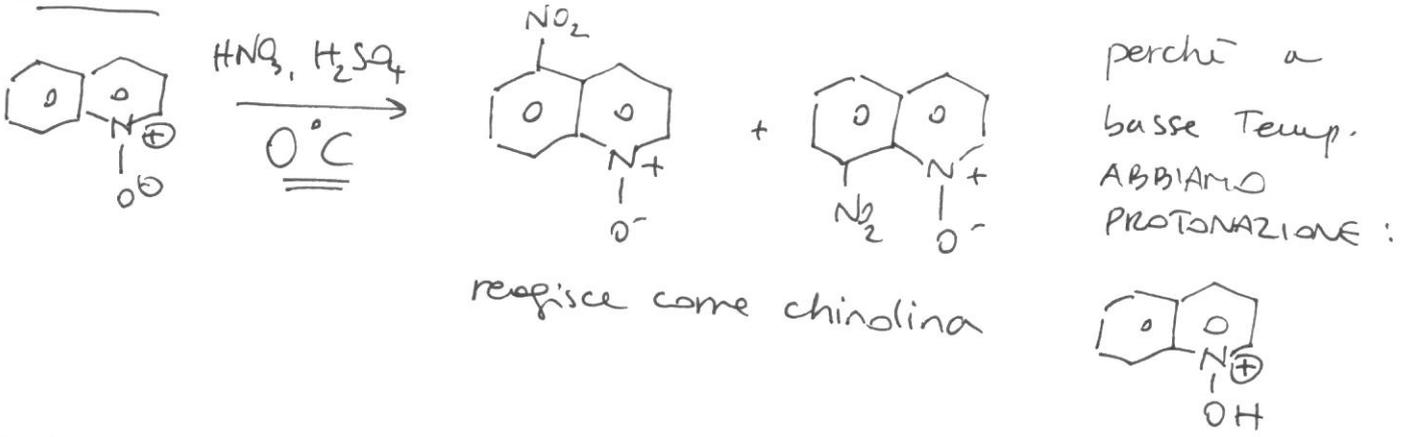
SOSTITUZIONI ELETTROFILI AROMATICHE SU N-OSSIDO!

Similmente alla piridina N-ossido, l'O con la sua carica negativa mi ATIVA LE POSIZIONI (2) e (4), POI DIPENDE DALLE CONDIZIONI...

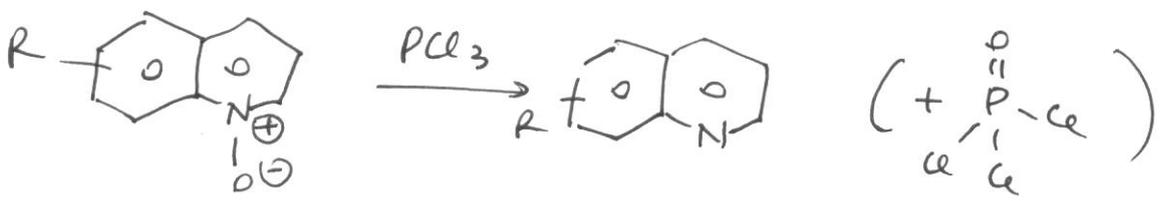
Per esempio:



INVECE:

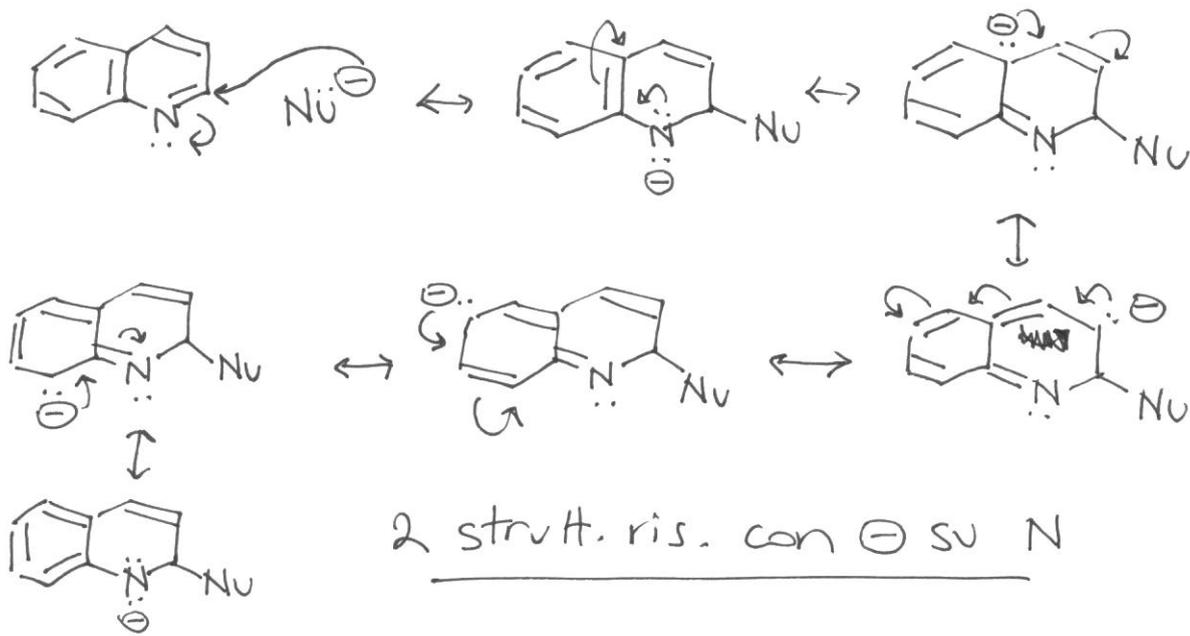


NB: PER RIOTTENERE CHINOLINA DOPO LA SOSTITUZIONE USO PCl3 COME PER LA PIRIDINA

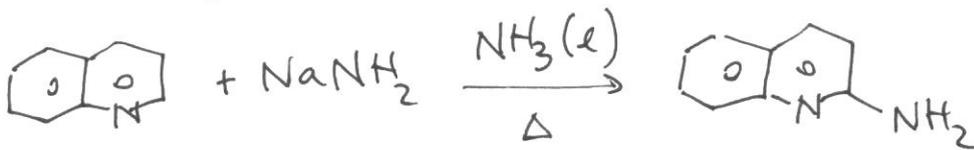


### ③ SOSTITUZIONE NUCLEOFILA AROMATICA

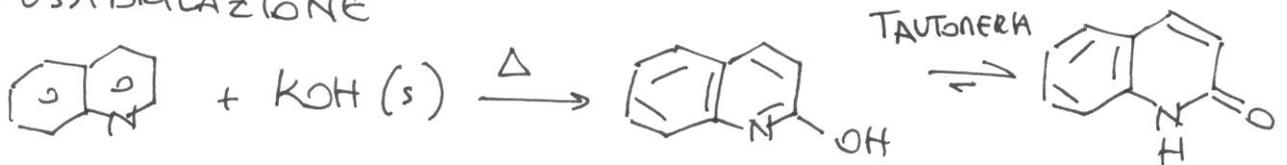
Grazie all' N su cui posso delocalizzare carica  $\ominus$  a seguito di attacco da Nu $\ominus$ , l'anello  $\Delta$ 20TATo e' + REATTIVO, specialmente in ② (o in ④ se la posizione ② e' occupata). (situaz. ~ piridina)



#### a) CHICIBABIN



#### b) OSSIDRILAZIONE

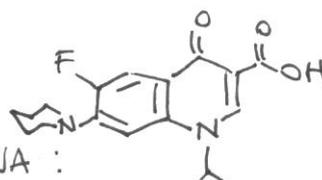
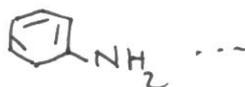
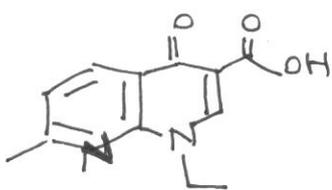


2-CHINOLONE

NB: 4-CHINOLONE IMPORTANTE: ACIDO NALDISSICO ANTIBATTERICO PER INFEZIONI VIE URINARIE

ANTIBIOTICI CHINOLONICI

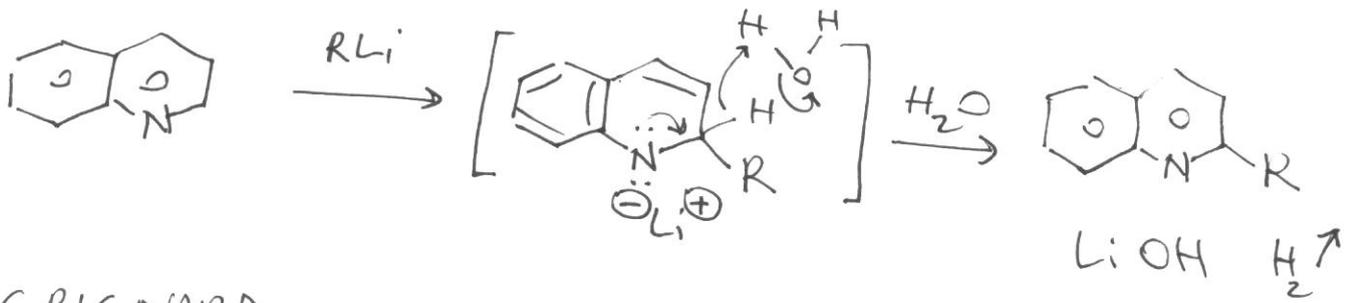
NON LO SINTETIZZO DA CHINOLINA, bensì:



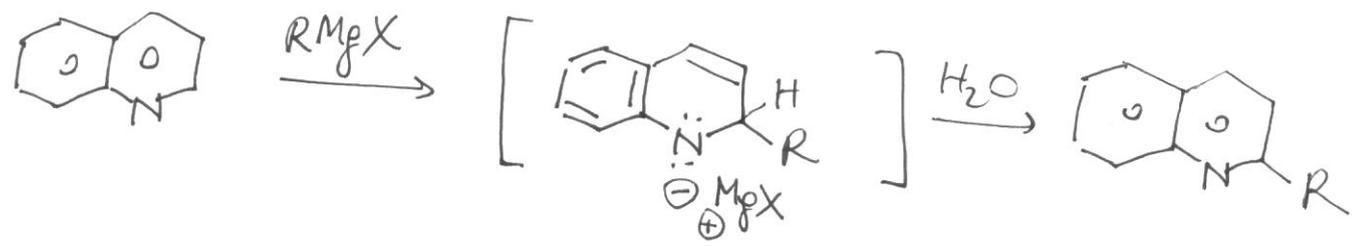
CIPROFLOSSACINA:

TAUTONERIA ~ PER 4-CHINOLONE invece tutte le altre posiz. restano prevalentemente forma FENOLICA

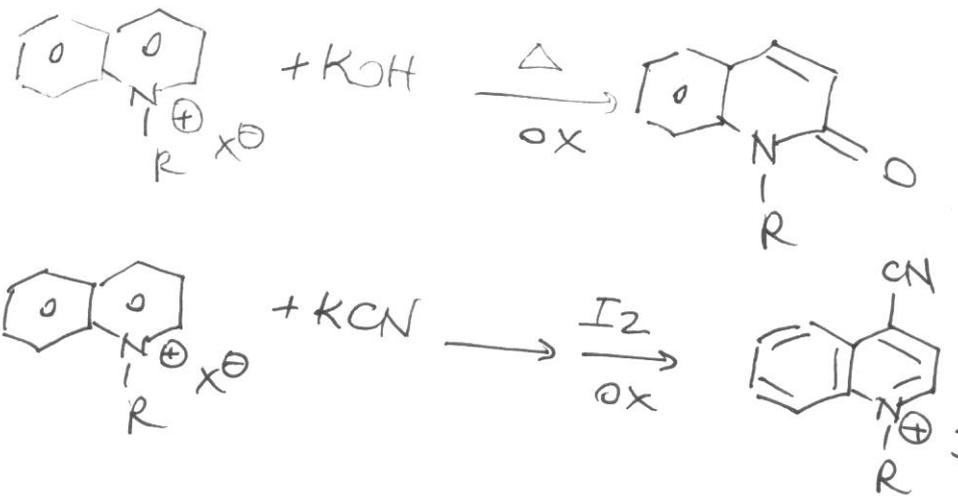
# ORGANOLITIO



# GRIGNARD



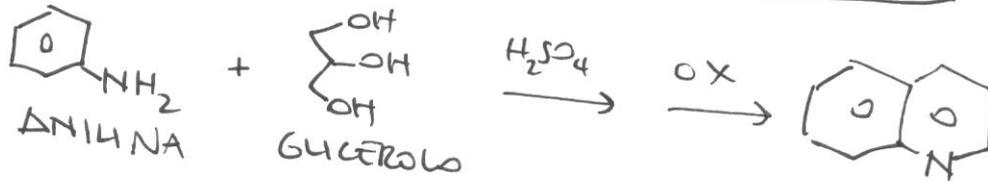
REAZIONI SU N-OSSIDI O SALI DI CHINOLINO  
 SOST. N<sup>+</sup>



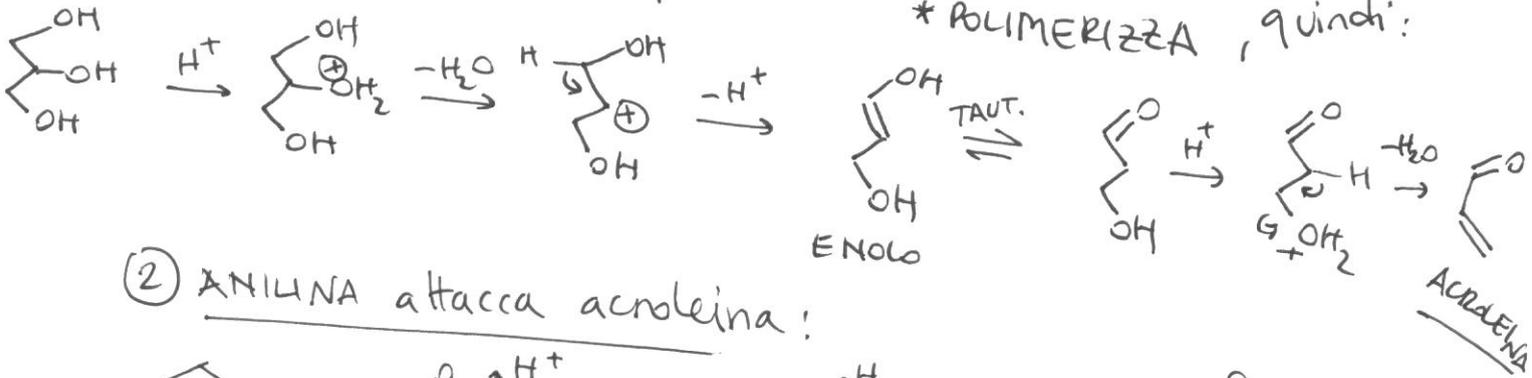
N-alkil-2-CHINOLONE  
 } serve un secondo passaggio di OX per avere prodotto di SOSTITUZIONE

# SINTESI DI SKRAUP DI $\varphi$ . (via CONNERCUALE)

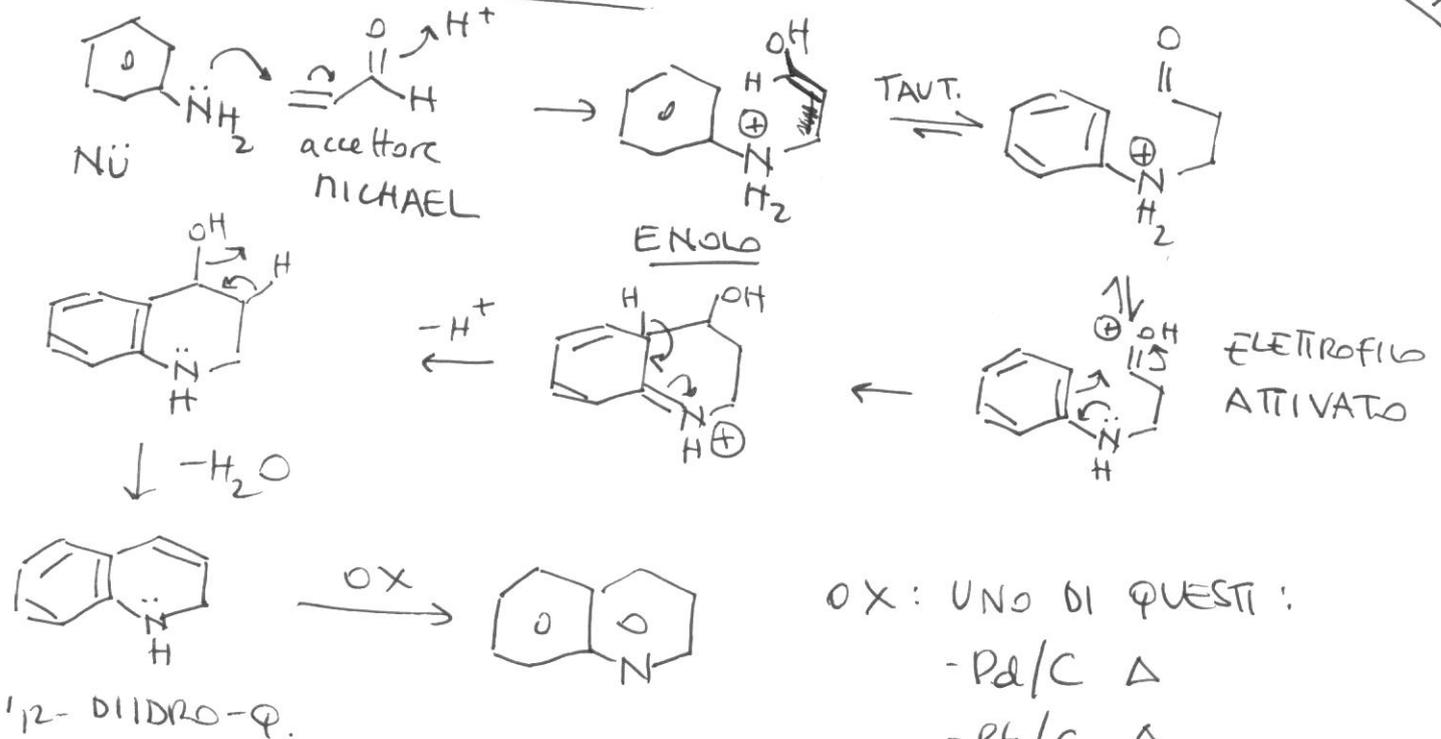
(9)



① L'anilina è Nü e reagisce con ACROLEINA che devo formare in situ dal glicerolo perché lei \*TOSSICA \*POLIMERIZZA, quindi:



② ANILINA attacca acroleina:



- OX: UNO DI QUESTI:
- Pd/C  $\Delta$
  - Pt/C  $\Delta$
  - c1ccc(cc1)[N+](=O)[O-] ecc.