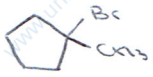
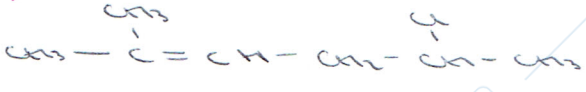
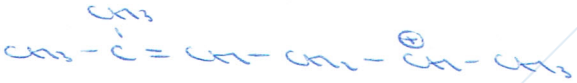
ejercicios tema 8

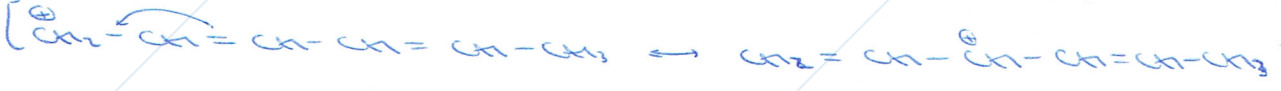
4. Tipo de haluro + carbocatión

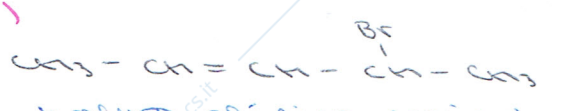
a)  haluro terciario 

b)  

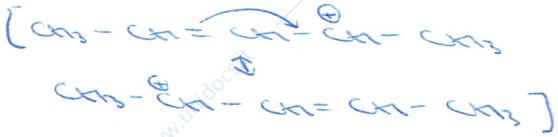
haluro secundario

c)  haluro alílico terciario

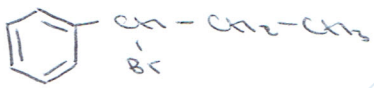


d) 

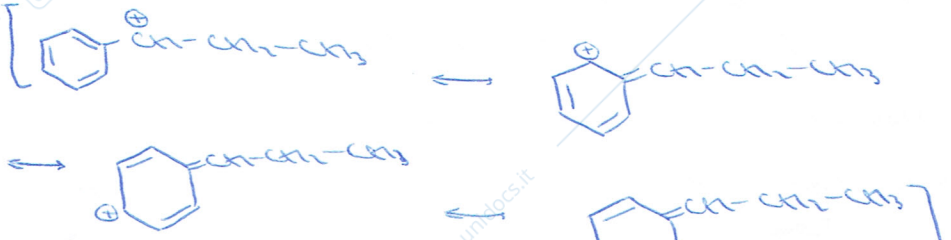
haluro alílico terciario



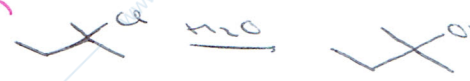
e)  haluro terciario 

f) 

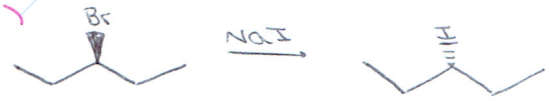
haluro bencílico



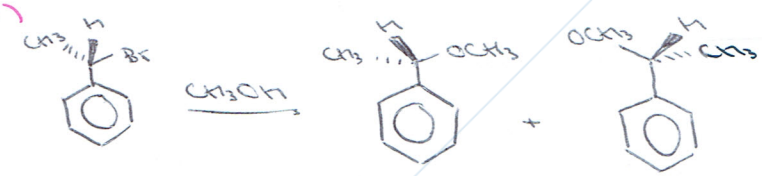
5. Reacción + probable (S_N1 / S_N2)

a) 

Se da S_N1 porque el nucleófilo es débil y el haluro terciario

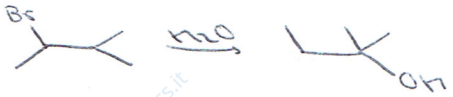
b) 

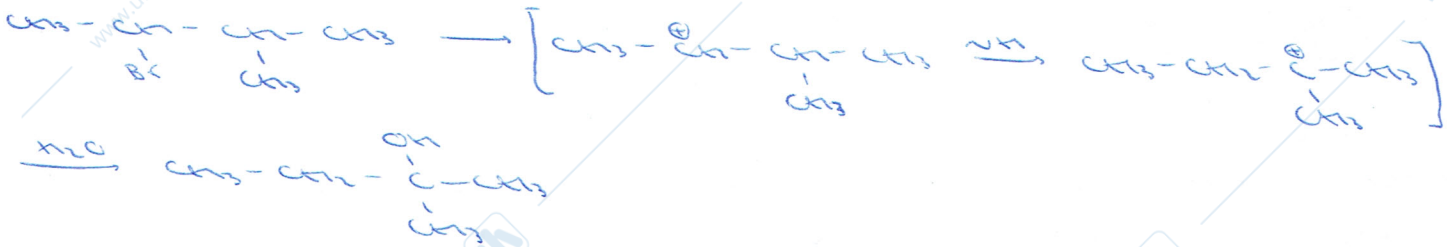
Se da S_N2 porque el I^- entra por la cara opuesta

c) 

Se da S_N1 porque el producto es una mezcla racémica

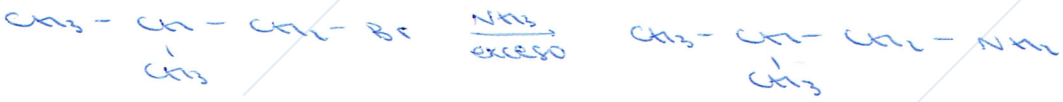
6. Mecanismo que justifique:



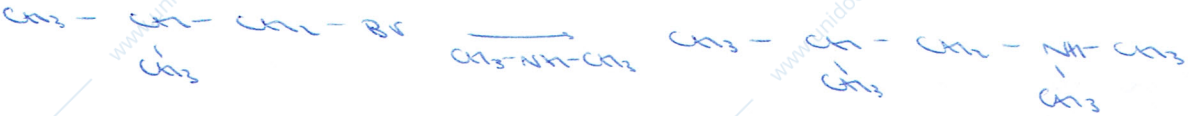


7. Bromuro de isobutilo con

a) NH_3 en exceso

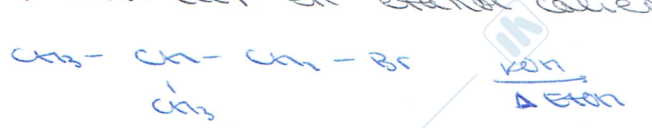


b) Dimetilamina en exceso

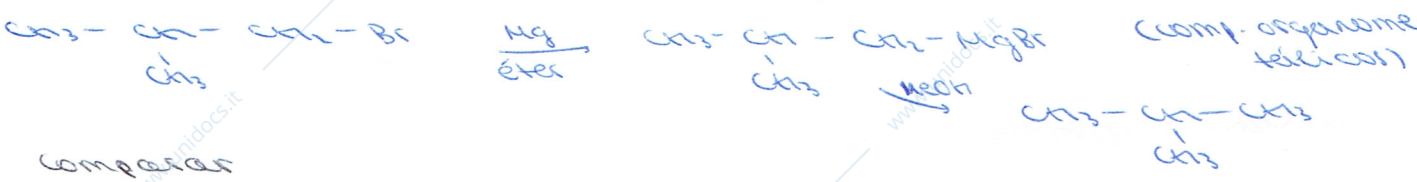


c) NaOH diluido

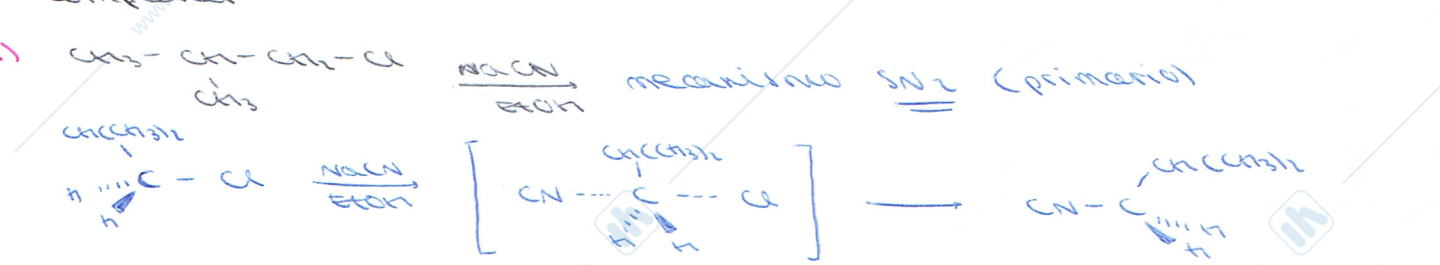
d) KOH (c) en etanol caliente

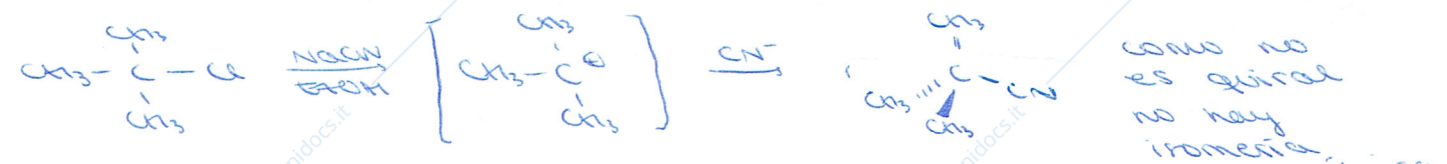


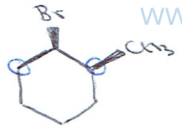
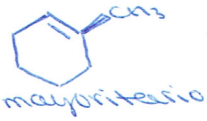
e) Mg en éter + adición metanal



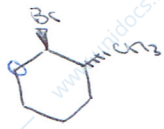
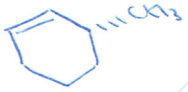
2. Comparar

a) 

b) 

b)   mayoritario +  E2

ambos H están anti respecto al Br, con lo cual se dan los 2 productos

solo un H de los C contiguos al α está anti respecto a Br

c) $CH_3-O-CH_2-Cl \xrightarrow[NaOCH_3]{NaOH}$ $[CH_3-\ddot{O}^{\oplus}-CH_2 \longleftrightarrow CH_3-\ddot{O}=CH_2]$

$\xrightarrow{CH_3O^-}$ $CH_3-O-CH_2-OCH_3$ Aunque sea primario se da S_N1 porque el carbo⊕ formado se estabiliza por resonancia

$CH_3-Cl \xrightarrow[NaOH]{NaOCH_3}$ OCH_3-CH_3 Mecanismo S_N2 (haluro de metilo)

3. Sust. nucleófila

a) $Br-CH_2=CH-CH_2-CH_3 \xrightarrow{NaCN}$ no se da

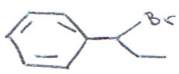
b) $Br-CH_2-CH=CH-CH_3 \xrightarrow{NaCN}$ $[{}^{\oplus}CH_2-CH=CH-CH_3 \leftrightarrow CH_2=CH-{}^{\oplus}CH-CH_3]$ S_N1

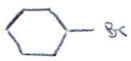
$CN-CH_2-CH=CH-CH_3 \xleftarrow{CN^-}$

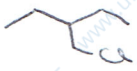
c) $CH_2=CH-CH_2-CH_2-Br \xrightarrow{NaCN}$ $CH_2=CH-CH_2-CH_2-CN$ S_N2

4. Eliminación

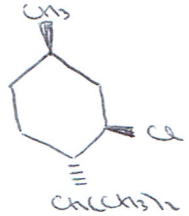
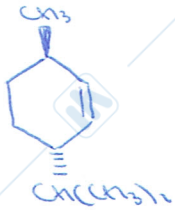
a)  $\xrightarrow{KOH}$  +  (mayoritario)

b)  $\xrightarrow{KOH}$  única posibilidad (E1)

c)  $\xrightarrow{KOH}$ 

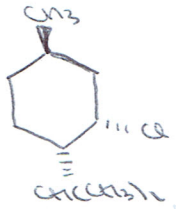
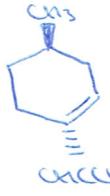
d)  $\xrightarrow{KOH}$  +  (mayoritario)

(E1 o E2) ↳ E1 (transposición)

8.  $\xrightarrow[E_1]{KOH}$ 

$CH(CH_3)_2$ $CH(CH_3)_2$

solo hay 1 producto porque el otro H del carbono β no está anti con respecto al Cl (no se puede dar E_2 por lo tanto)

 $\xrightarrow{KOH}$  + 

$CH(CH_3)_2$ $CH(CH_3)_2$ $CH(CH_3)_2$

este puede ser tanto E_2 como E_1

9. $CH_2=CH-\underset{Cl}{CH}-CH_3 \xrightarrow{NaCN}$ A, B, C y D

A, B, C → isómeros tienen N

D → no tiene N (es conjugado)

A, B, C → sustitución

D → eliminación

$CH_2=CH-\underset{Cl}{CH}-CH_3 \xrightarrow{NaCN} CH_2=CH-CH=CH_2$ (D)

$CH_2=CH-\underset{Cl}{CH}-CH_3 \xrightarrow{NaCN}$ se da por SN1 porque el carbocatión formado es alílico

$\left[CH_2=CH-\overset{\oplus}{C}H-CH_3 \longleftrightarrow \overset{\oplus}{C}H_2-CH=CH-CH_3\right]$

$\downarrow CN^-$

$CH_2=CH-\underset{CN}{CH}-CH_3$ (A) (B)

$CH_2-\underset{CN}{CH}=CH-CH_3$ (C) (no es quiral)

ejercicios tema 19

1. Productos de 1-butanol con

a) PBr_3

$CH_3-CH_2-CH_2-CH_2-OH \xrightarrow{PBr_3} CH_3-CH_2-CH_2-CH_2-Br$ — S_N2 siempre

b) H_2SO_4(cc) Δ

$CH_3-CH_2-CH_2-CH_2-OH \xrightarrow[\Delta]{H_2SO_4} CH_3-CH_2-CH=CH_2$ — E_2

c) K

$CH_3-CH_2-CH_2-CH_2-OH \xrightarrow{K} CH_3-CH_2-CH_2-CH_2-O^{\ominus}\ K^{\oplus}$

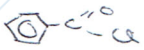
d) CrO_3, Py

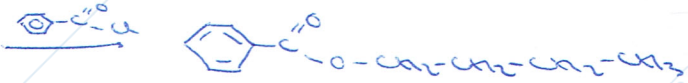
$CH_3-CH_2-CH_2-CH_2-OH \xrightarrow[Py]{CrO_3}$ 

(oxidación que para en aldehído)

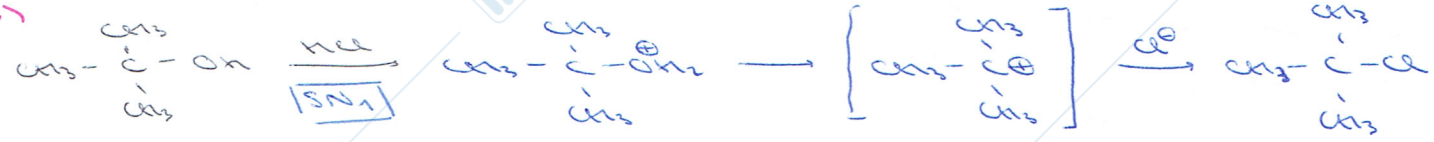
e) $K_2Cr_2O_7$ ácido

$CH_3-CH_2-CH_2-CH_2-OH \xrightarrow[\text{ácido}]{K_2Cr_2O_7}$ 

f) 

$CH_3-CH_2-CH_2-CH_2-OH \xrightarrow{}$ 

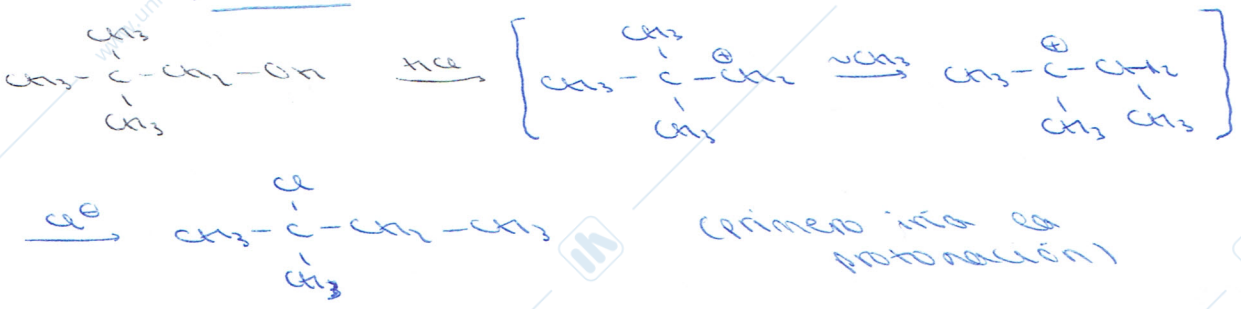
2. Reacción con HCl

a) 

S_N1

b) 

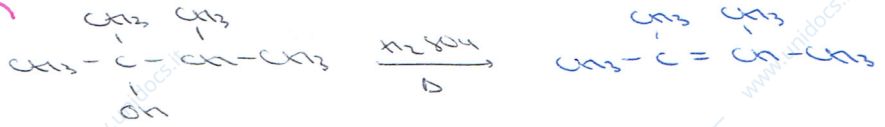
S_N1 o S_N2

c) 

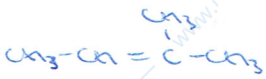
(primero irá la protonación)

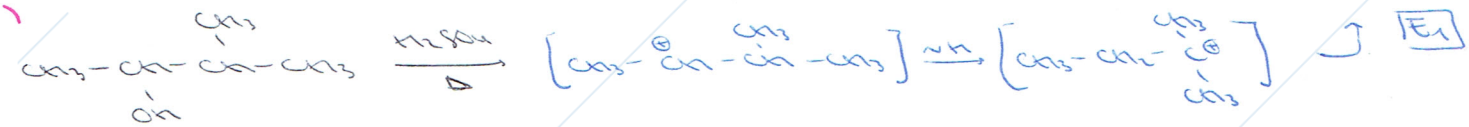
d) $CH_3-CH_2-CH_2-CH_2-CH_2OH \xrightarrow[S_N2]{HCl} CH_3-CH_2-CH_2-CH_2-CH_2-Cl$

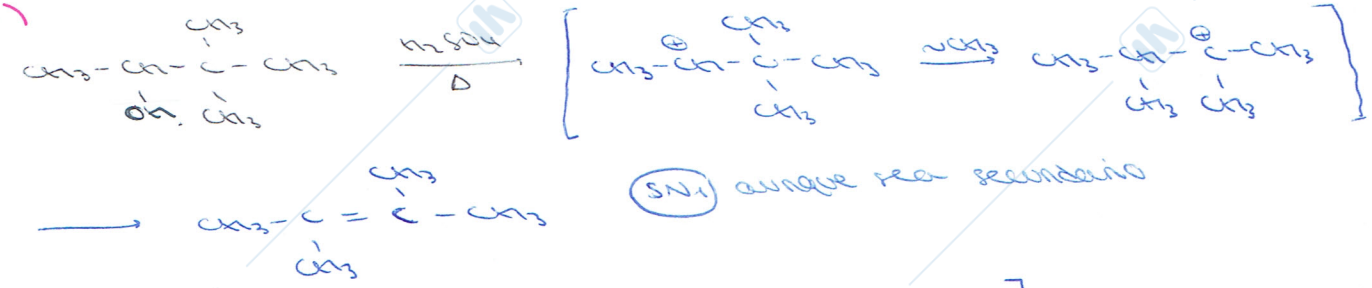
3. Deshidratación

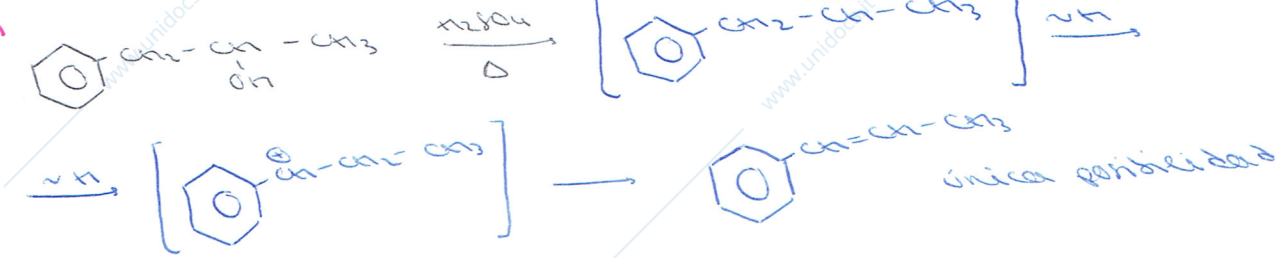
a) 

(+ sustituida)

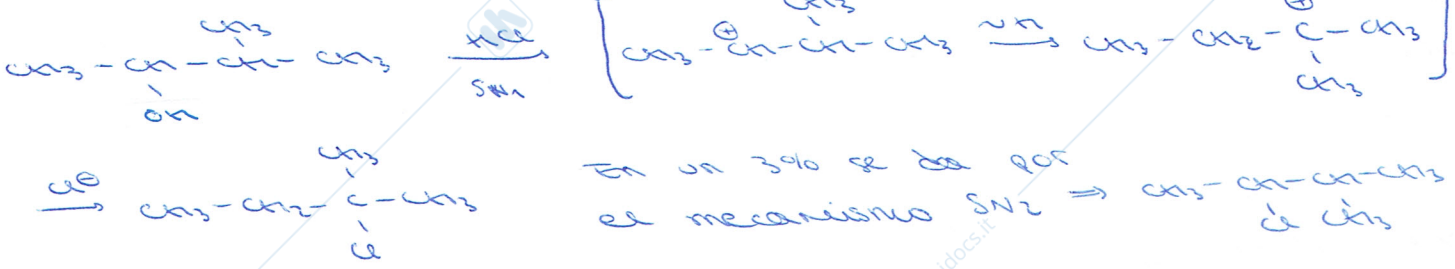


b) 

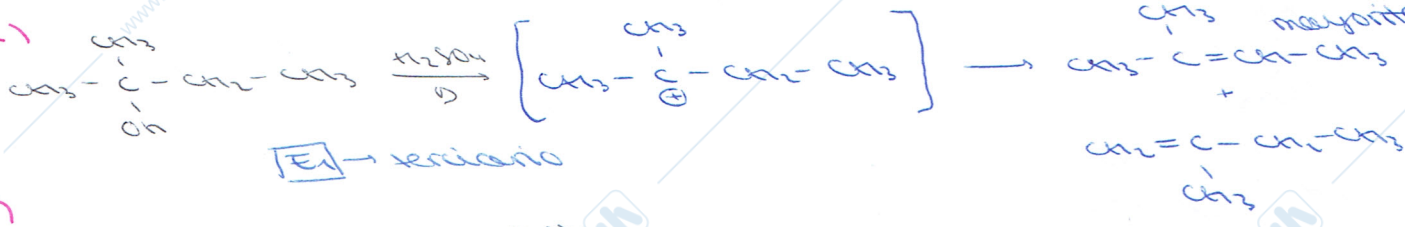
c) 

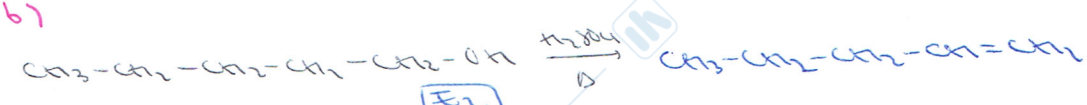
d) 

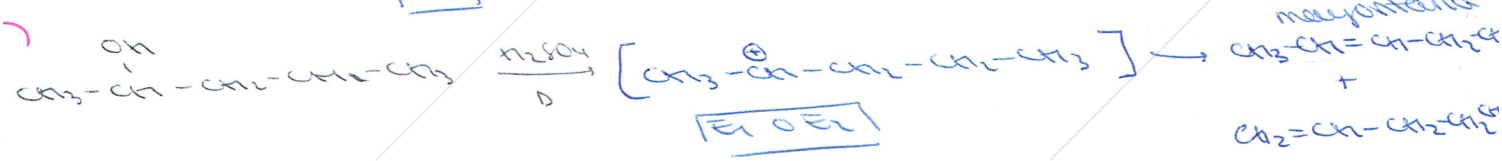
4. 3-metil-2-butanol con HCl

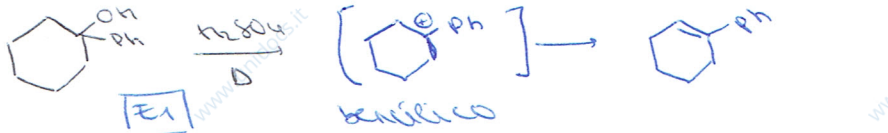


5. Deshidratación en medio ácido

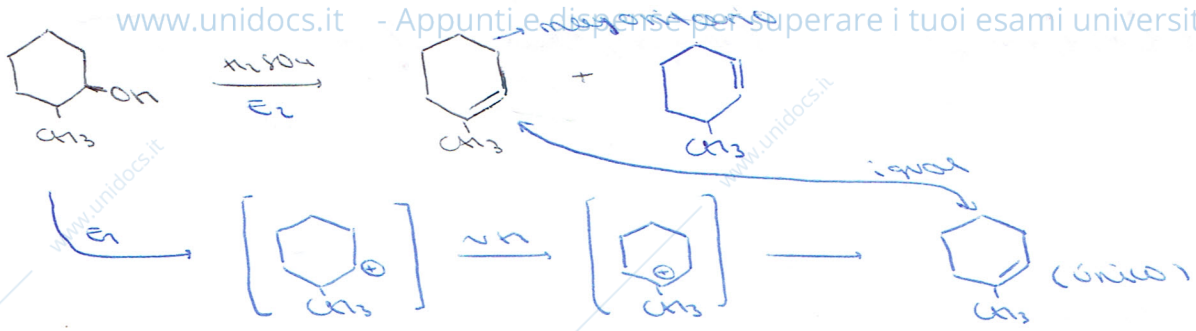
a) 

b) 

c) 

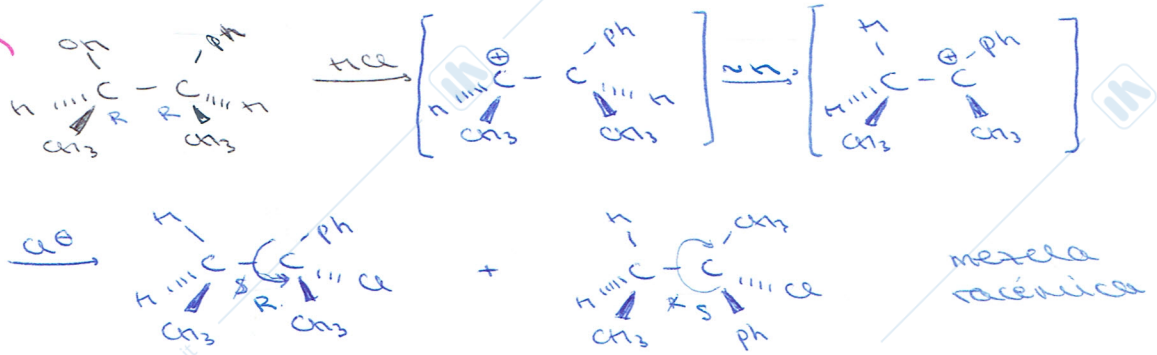
d) 

6)

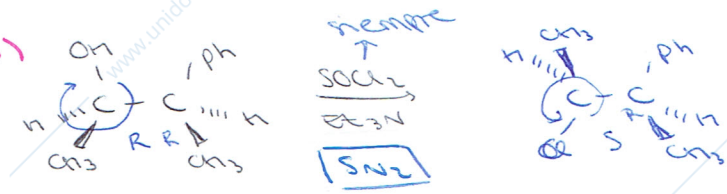


b. Meccanismo

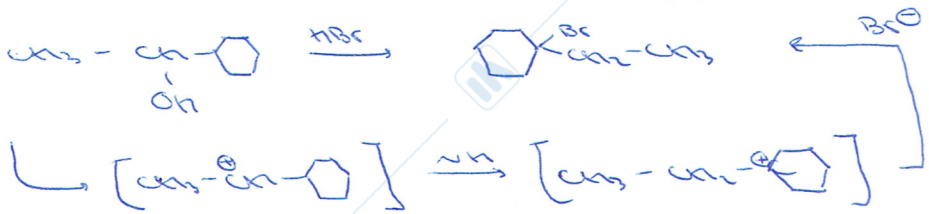
a)



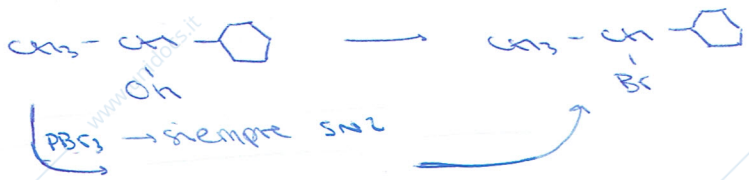
b)



7. 1-cicloexanol + HBr ⟶ 1-etilciclohexano
(1-bromo)

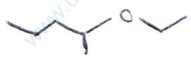


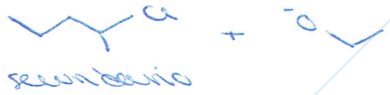
b) 1-ciclohexiletanol ⟶ 1-bromo-1-ciclohexiletano



ejercicios tema 11

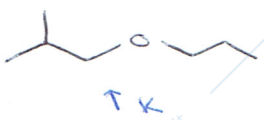
1. Alcohol más adecuado para síntesis de Williamson

a) 

Opción 1: 
secundario

Opción 2: 
primario ⟹  2-pentanol

mejor porque nunca da E (casi)

b) 

Opción 1 → 

Opción 2 → 

valen ambas (primarios)

 (2-metil-1-etanol) o  (1-etanol)

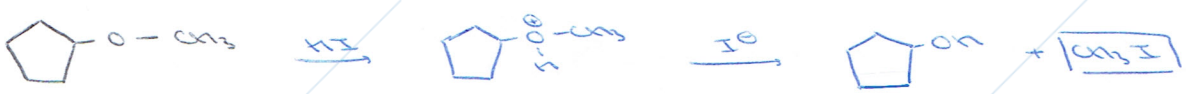
c) 

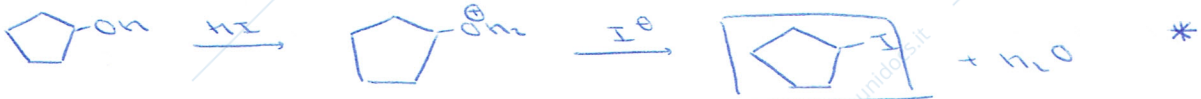
Opción 1:  } solo éter

Opción 2: 

 (terc-butanol)

2. Tratamiento con (un mol) de HI (exceso)

a) 

 *

b) 

(siguiendo lo mismo que antes)

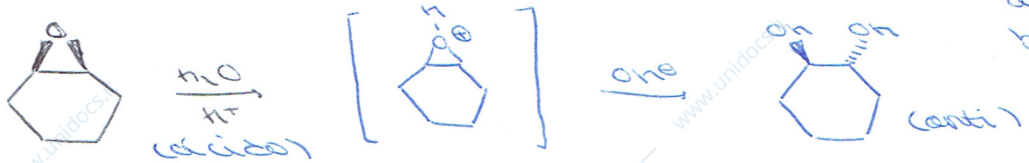
c)  (pasos intermedios)

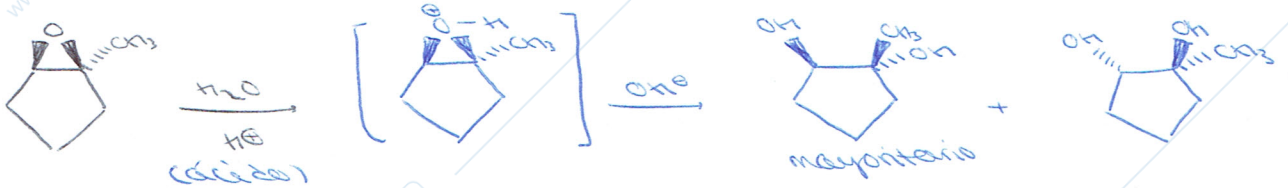
d)  (no sigue la reacción porque el alcohol es un fenol)

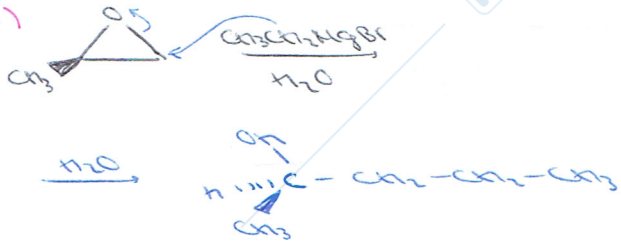
* Puede seguir otro camino

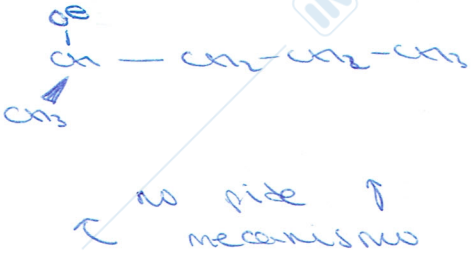
3. Completar

ácido → + sustituido
básico → - sustituido

a) 

b) 

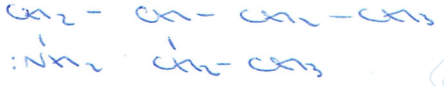
c) 



ejercicios tema 12

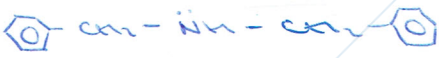
1. Formular

a) 2-etil-1-butanamina



b) N-etil-1-butanamina

c) Dibencilamina



d) 2,2-dimetil-1,3-propanodiamina

2. Orden creciente de basicidad

a) Amoniaco, anilina, metilamina

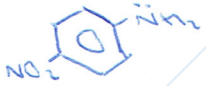
② NH_3

③ 
↳ por el N está deslocalizado sobre el anillo aromático

CH_3-NH_2 ① → por efecto inductivo estabiliza la carga ⊕ de la sal

b) Anilina, 4-nitroanilina, 4-metoxianilina

② 

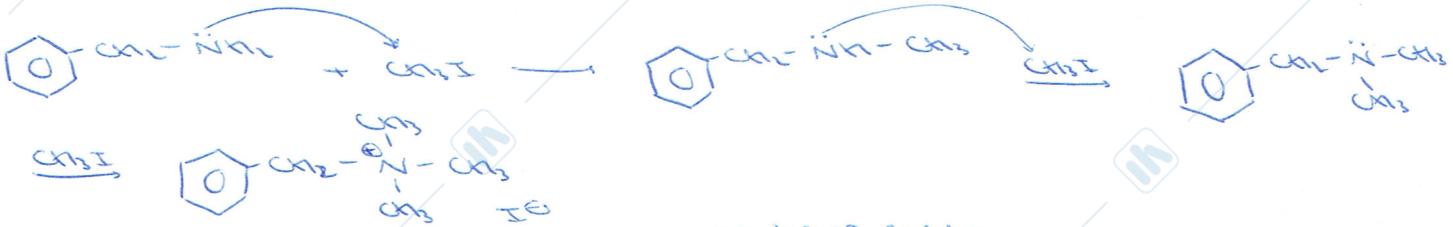


3. Bencilamina $C_6H_5-CH_2-NH_2$:

a) Cloruro de acetilo

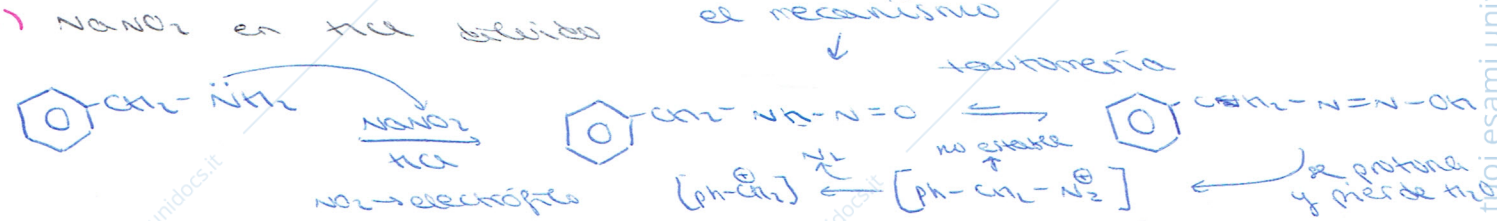
(no es soluble)

b) CH_3I en exceso



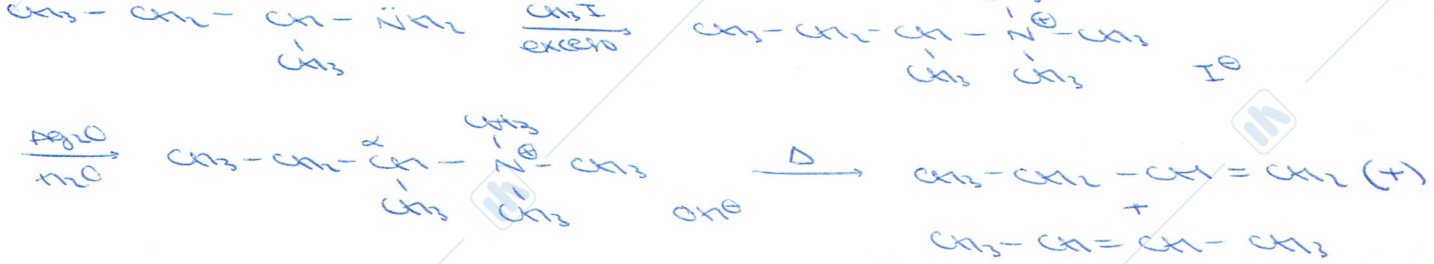
c) $NaNO_2$ en HCl diluido

no hace falta el mecanismo

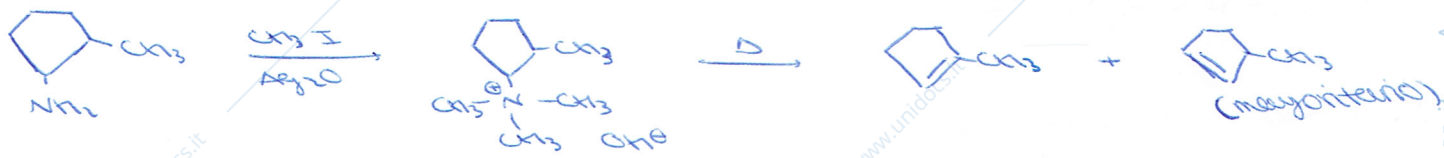


4. Eliminación de Hofmann (CH_3I en exceso, Ag_2O, Δ)

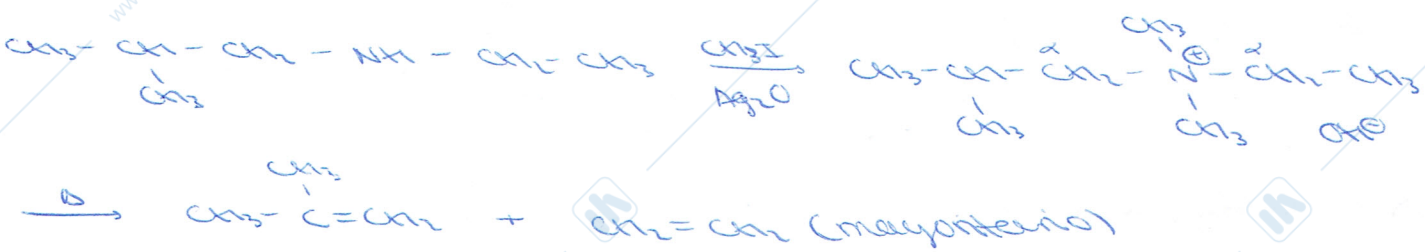
a) sec-butilamina



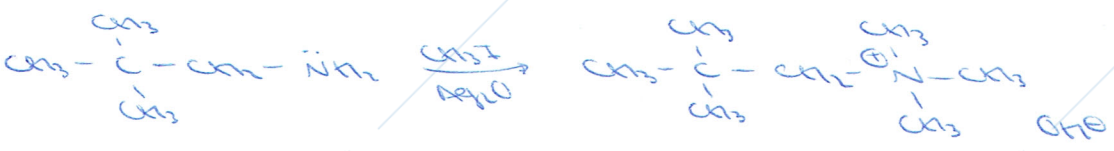
b) 2-metilciclopentilamina



c) N-etil-isobutilamina

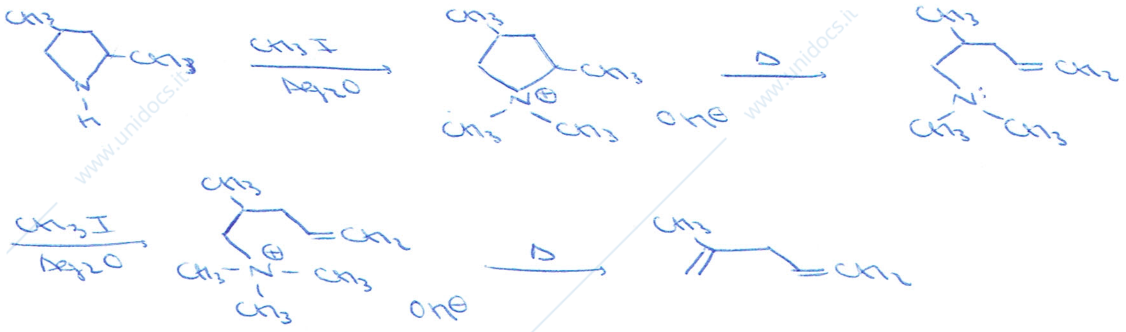


e) Neopentilamina



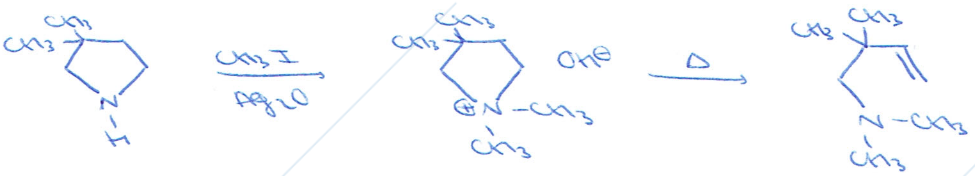
Δ → no se da porque el C β no tiene H's

d) 2,4- dimetilpirrolidina

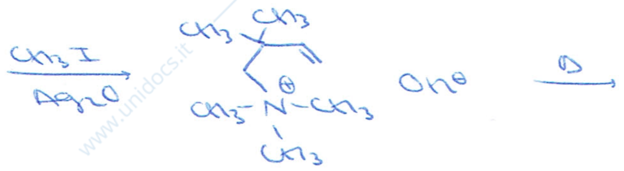


como sigue teniendo N puede seguir reaccionando

f) 3-3- dimetilpirrolidina



puede seguir



no puede seguir porque el C β no tiene H libres

$CH_3-\ddot{N}H_2$ $\quad$ $CH_3-\ddot{N}H-CH_3$ $\quad$ $CH_3-\ddot{N}(CH_3)-CH_3$

$CH_3\rightarrow\overset{\oplus}{N}H_3$ $\quad$ $CH_3\rightarrow\overset{\oplus}{N}H_2\leftarrow CH_3$ $\quad$ $CH_3\rightarrow\overset{\oplus}{N}H(\uparrow CH_3)\leftarrow CH_3$

- Por efecto inductivo la última amina sería más básica
- Solvatación → $CH_3-\ddot{N}H_2$ más fácil por tener menos impedimentos, entonces es más básica

Conclusión → basicidad de alquilaminas semejante (por efectos contrarios que se compensan)