Lista de Exercícios - Substituição nucleofílica, eletrofílica e radicalar

1)

(a) $(CH_3)_2N^{\ominus}$

Ao comparamos o mesmo átomo atacante, a nucleofilicidade acompanha a basicidade. $(CH_3)_2N^{\ominus}$ é mais básico que $(CH_3)_2NH$. $(CH_3)_2N^{\ominus}$ tem maior facilidade de doar um par eletrônico a um átomo de C do que $(CH_3)_2NH$, pois um N com carga negativa é mais poderoso que o protonado.

(b) $(CH_3)_3B$. Para N de mesmo período, a ordem de nucleofilicidade acompanha a ordem de basicidade.

(c) H_2S. Enxofre é mais volumoso que oxigênio, sendo mais difícil de ser solvatado o H_2S em relação à H_2O, daí a maior nucleofilicidade do H_2S.

(d) $CH_3S^{\ominus}$. $CH_3S^{\ominus}$ é mais polarizável que $Cl^{\ominus}$, sendo, portanto, melhor nucleófilo.

2) $(CH_3)_3CCl < (CH_3)_2CHCl < CH_3Br < CH_3OTs$

3)

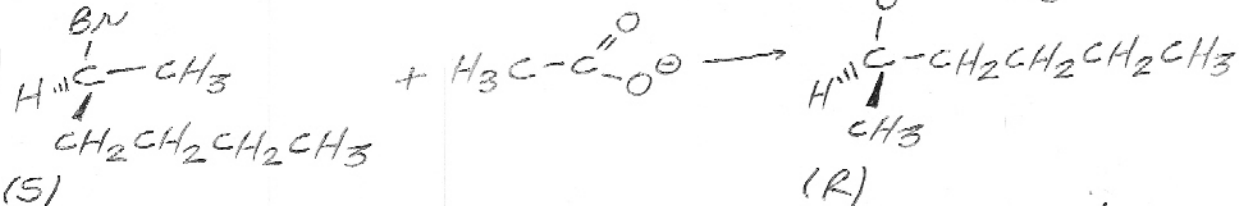
(a) iodeto de metila

(b) iodeto de metila em clorofórmio

(c) 2-cloropropano

(d) brometo de alila

4)

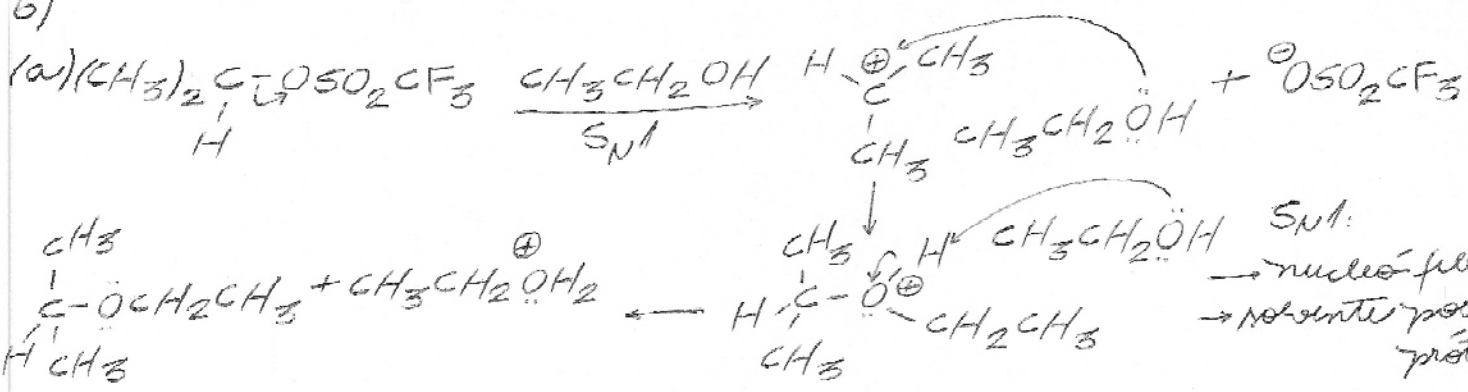


(S) (R)

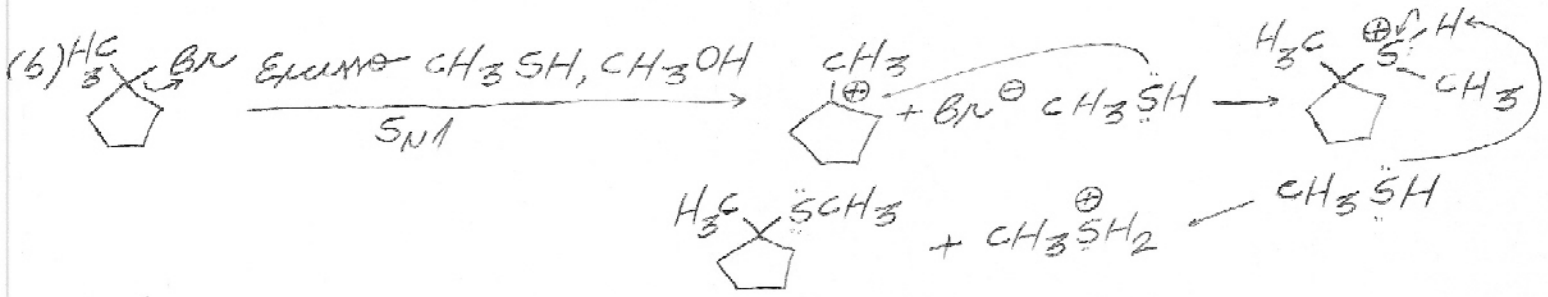
Essa reação ocorre via S_N2 e, portanto, ocorre inversão de configuração.

5) $H_2C=CHBr < CH_3CH_2Br < H_3CCH(Br)CH_3 < H_2C=CHCH(Br)CH_3$

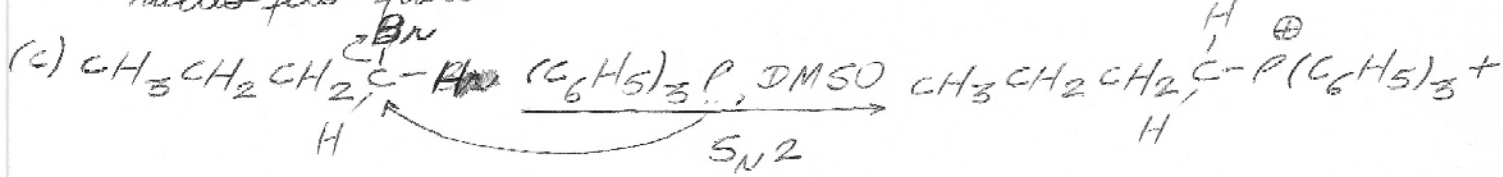
6)

(a) 

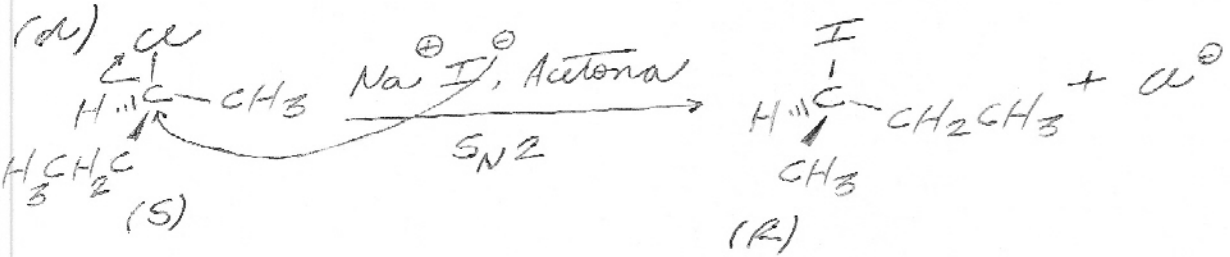
S_N1:
→ nucleófilo fraco
→ solvente polar prótico

(b) 

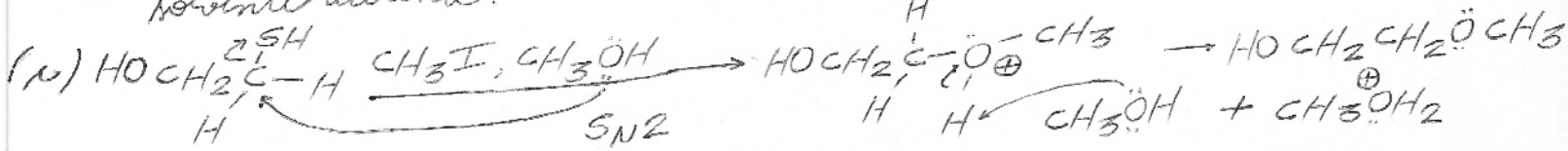
S_N1:
→ haleto de alquila 3° ;
→ solvente polar prótico ;
→ nucleófilo fraco

(c) 

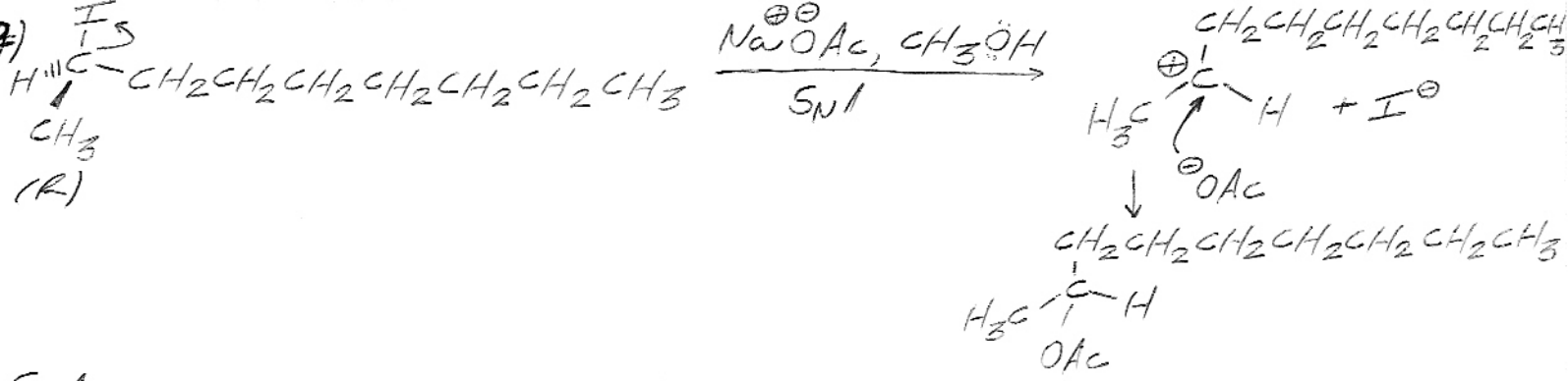
S_N2:
→ haleto de alquila 1°
→ solvente DMSO

(d) 

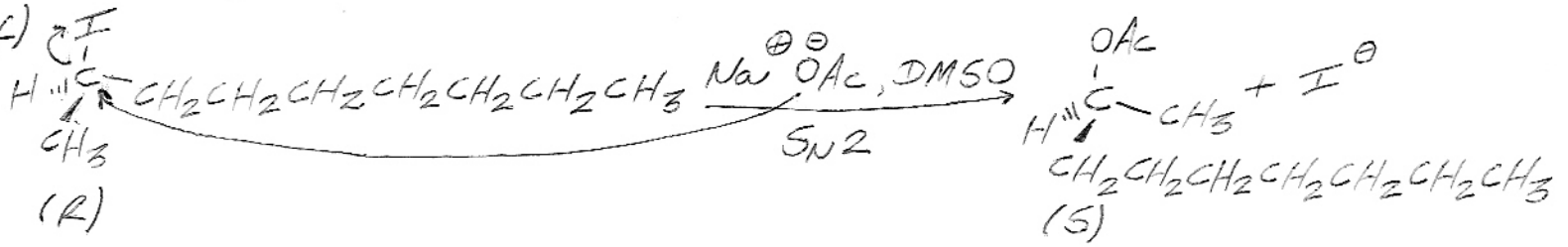
S_N2:
→ nucleófilo forte ;
→ solvente acetona.

(e) 

S_N2:
→ substrato 1°

(g) 

S_N1:
→ haleto de alquila 2° de cadeia longa; S_N1 favorecida pelo uso de solvente polar prótico

(f) 

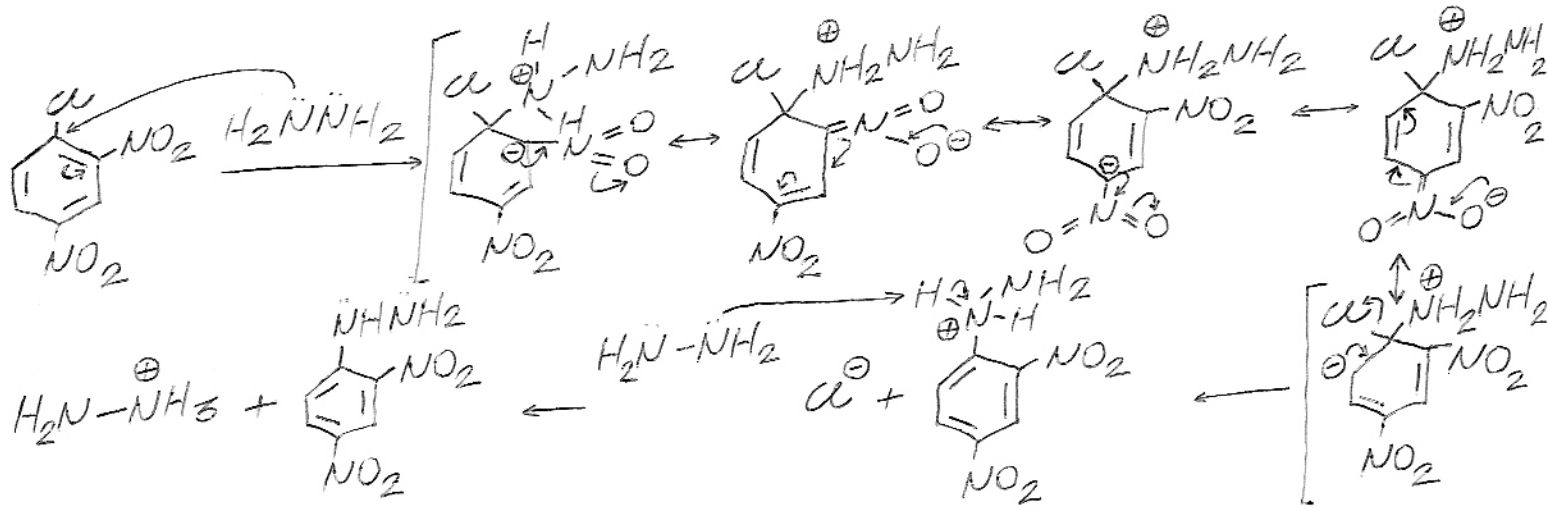
(R)

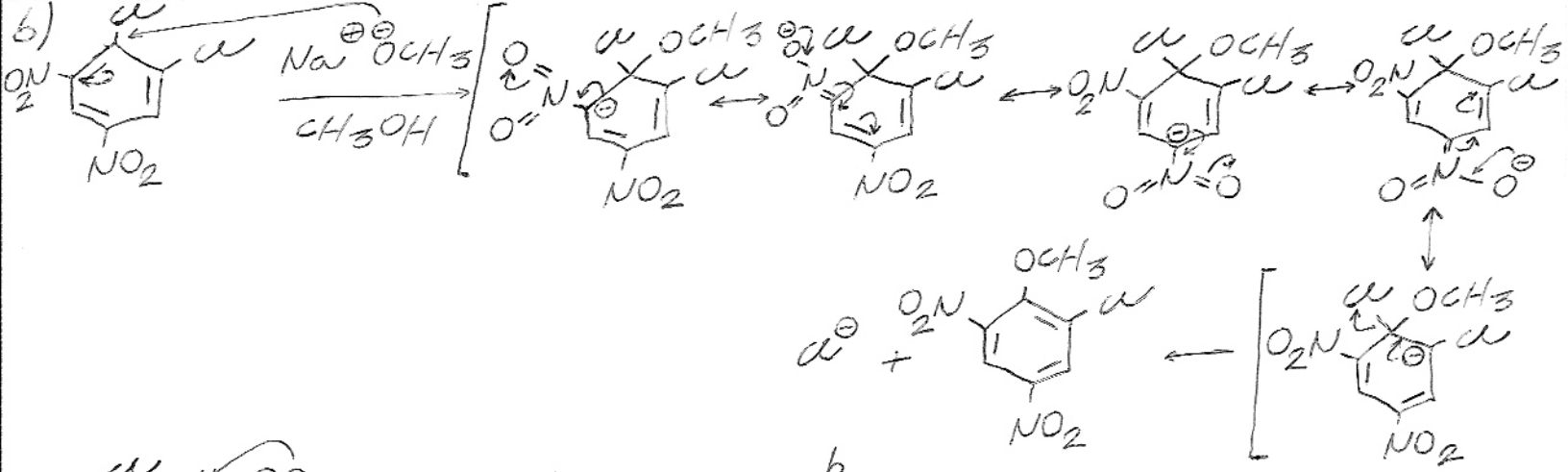
(S)

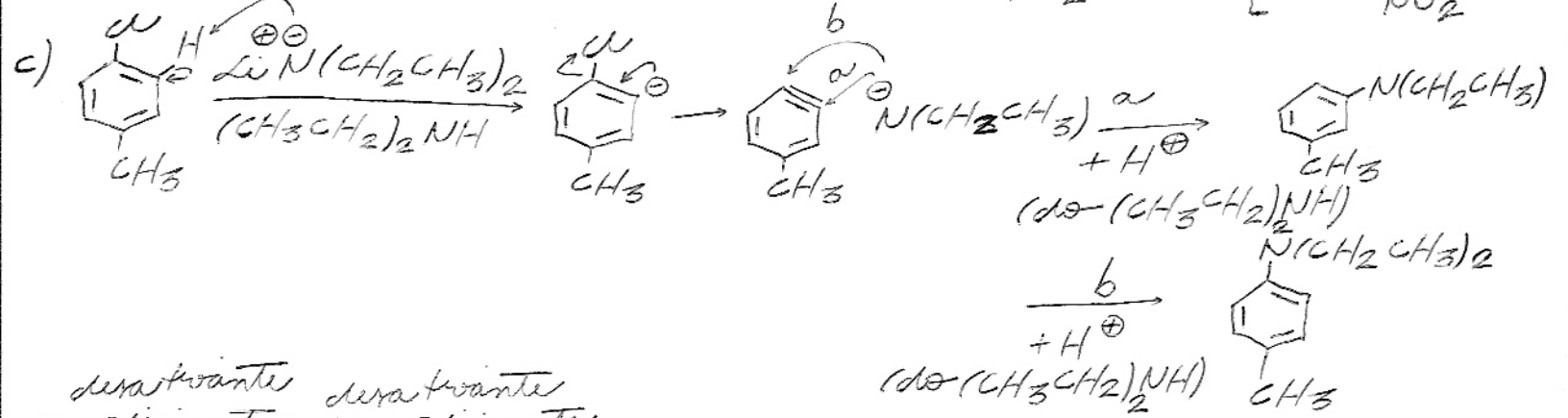
S_N2:
→ haleto de alquila 2° com S_N2 favorecida pelo uso de DMSO como solvente

7) 

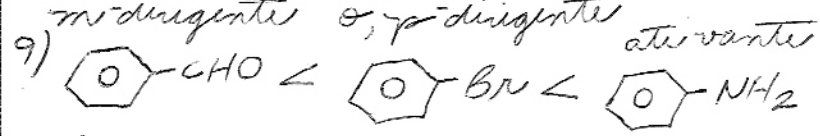
8)

a) 

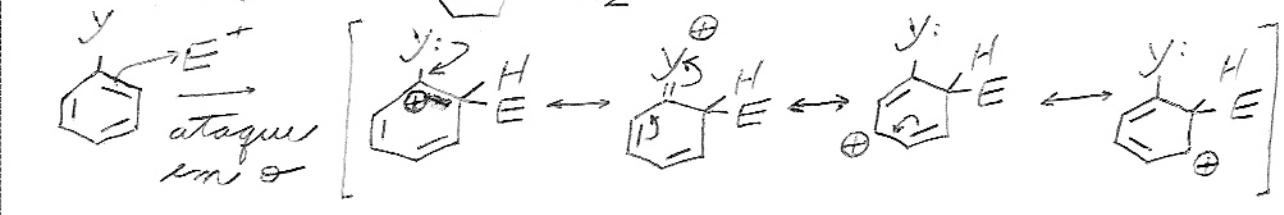
b) 

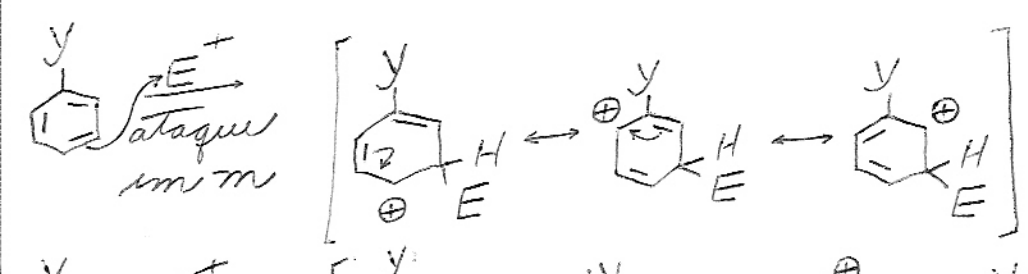
c) 

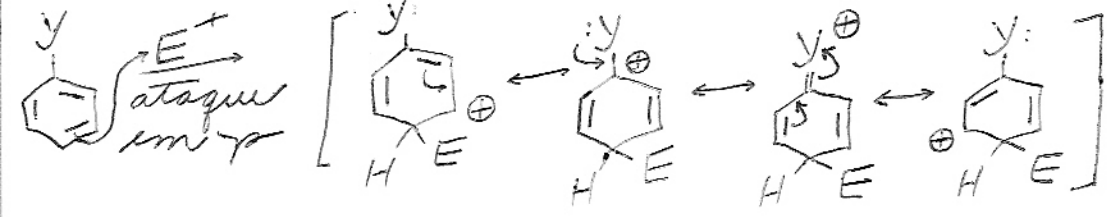
g) desativante m-dirigente < desativante o, p-dirigente < ativante

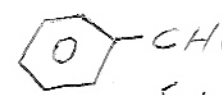


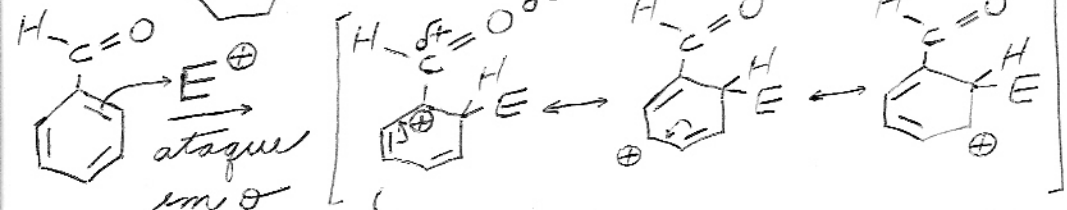
Para  e :



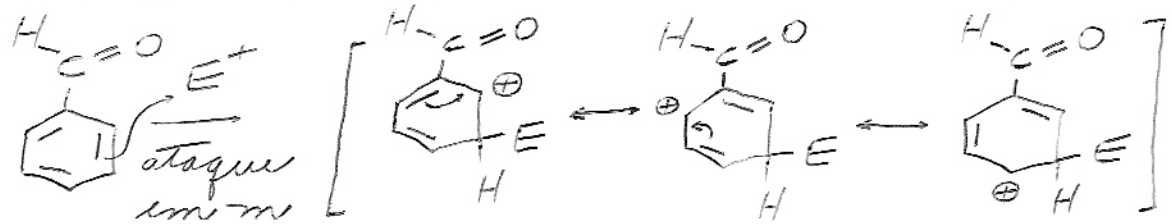


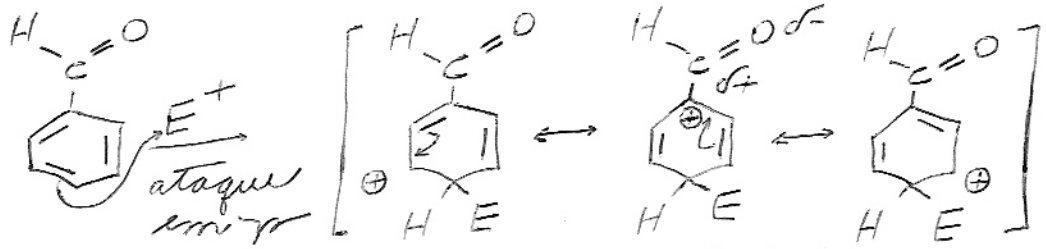


Para  :



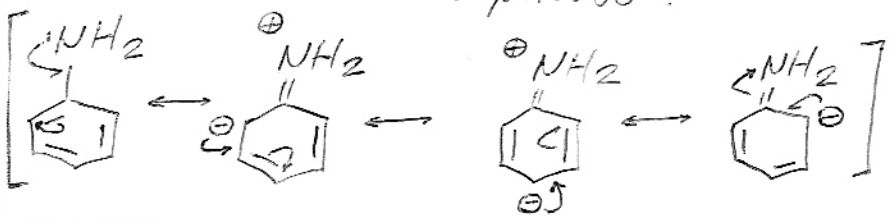
↳ desestabiliza o intermediário



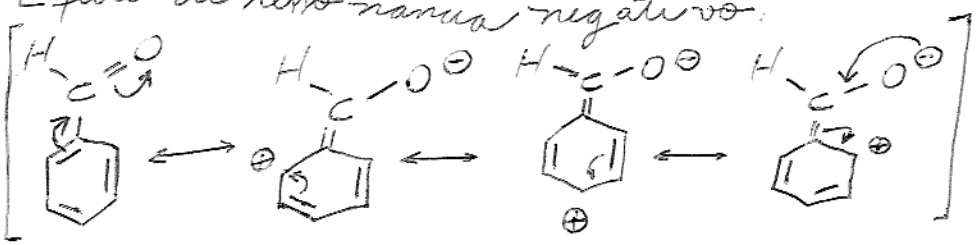


desestabiliza o intermediário

Efeito de ressonância positivo:

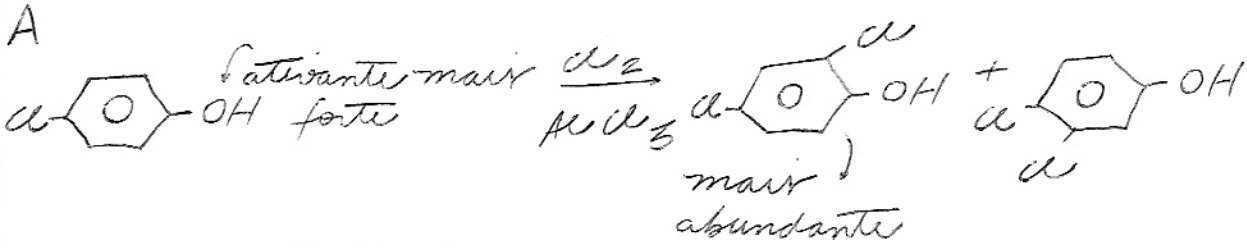


Efeito de ressonância negativo:



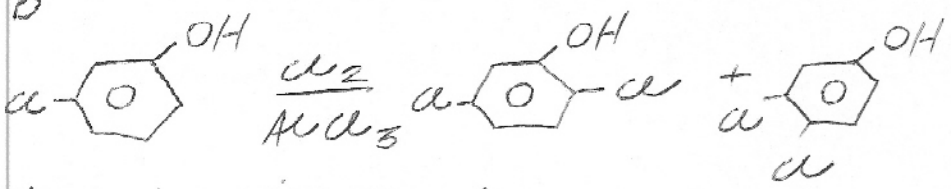
11)

A



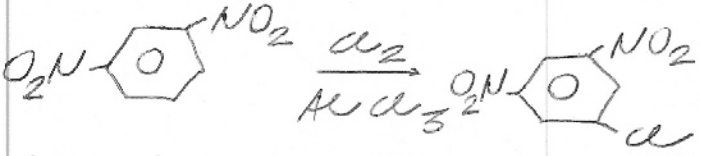
o grupo –OH é ativante mais forte que –Cl; os dois substituintes são o, p-direcionantes, porém a orientação será aquela de acordo com o grupo mais ativante.

b



os dois substituintes são o, p-dirigentes e induzem a substituição a ocorrer nas mesmas posições do anel. É difícil a formação de benzenos 1,2,3-trissubstituídos.

c



os dois grupos nitro são meta dirigentes e induzem a substituição no mesmo átomo de C do anel.

12)

a) acetanilida

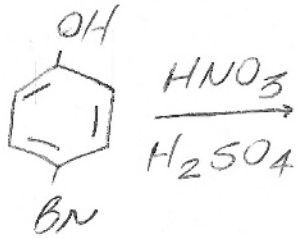
b) anilina

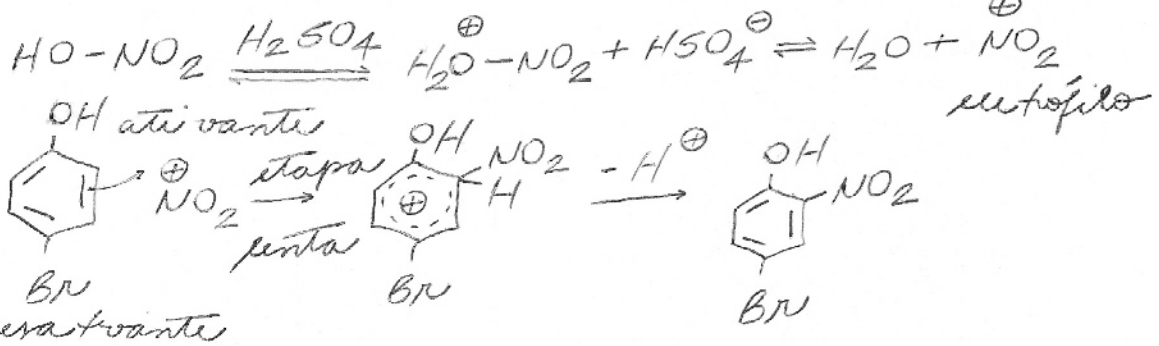
c) p-metoxitolueno

d) m-nitrotolueno

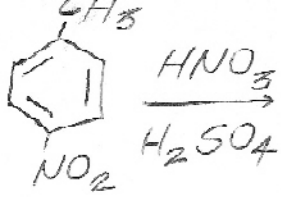
13)

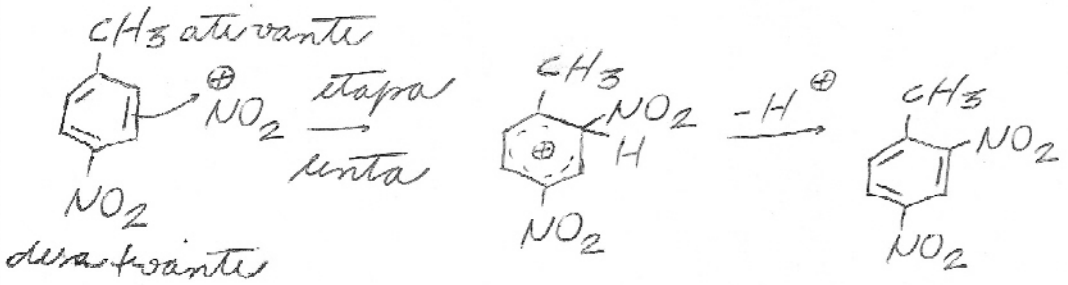
a)



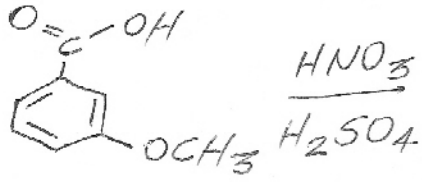


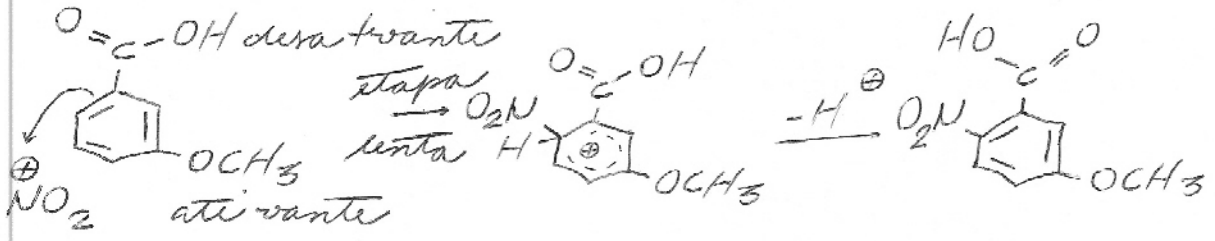
b)



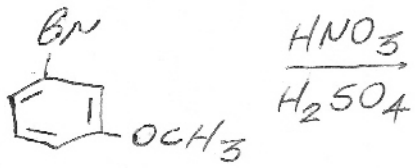


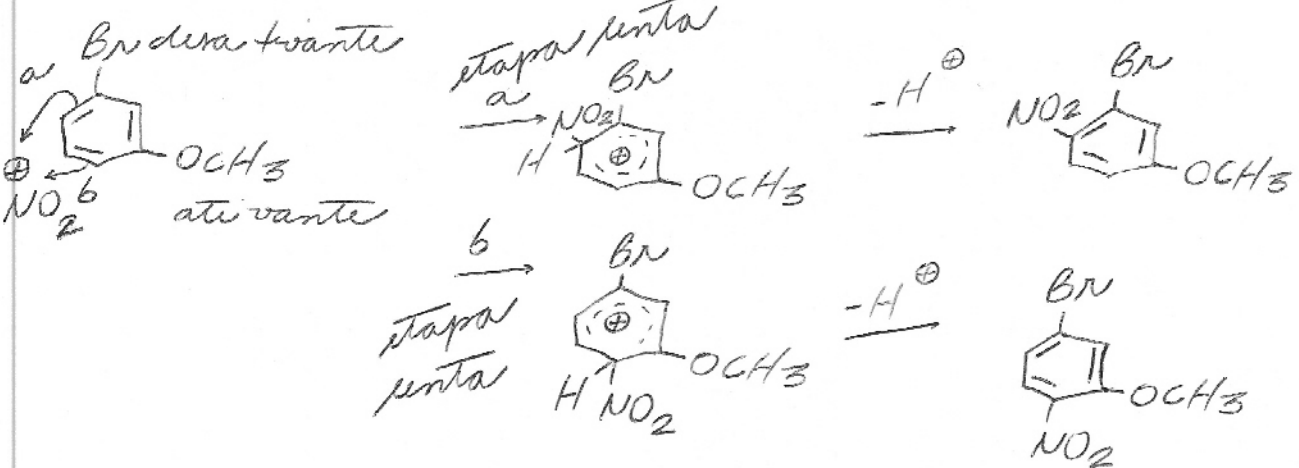
c)





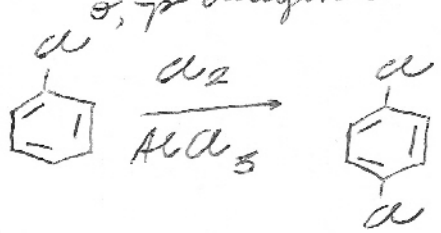
d)



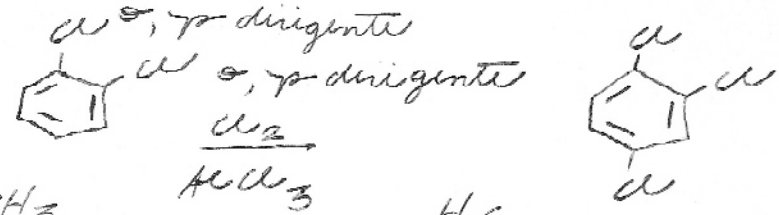


14)

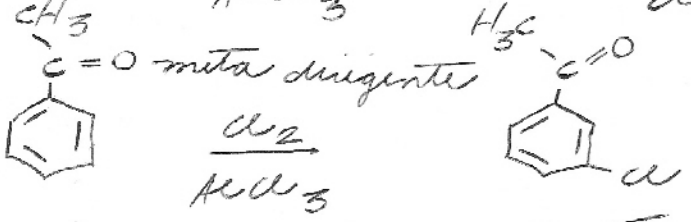
a) o, p dirigente

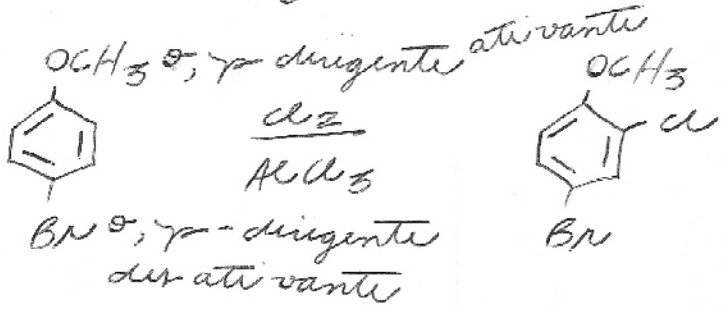


para-substituição predomina dado o efeito indutivo do grupo -Cl.

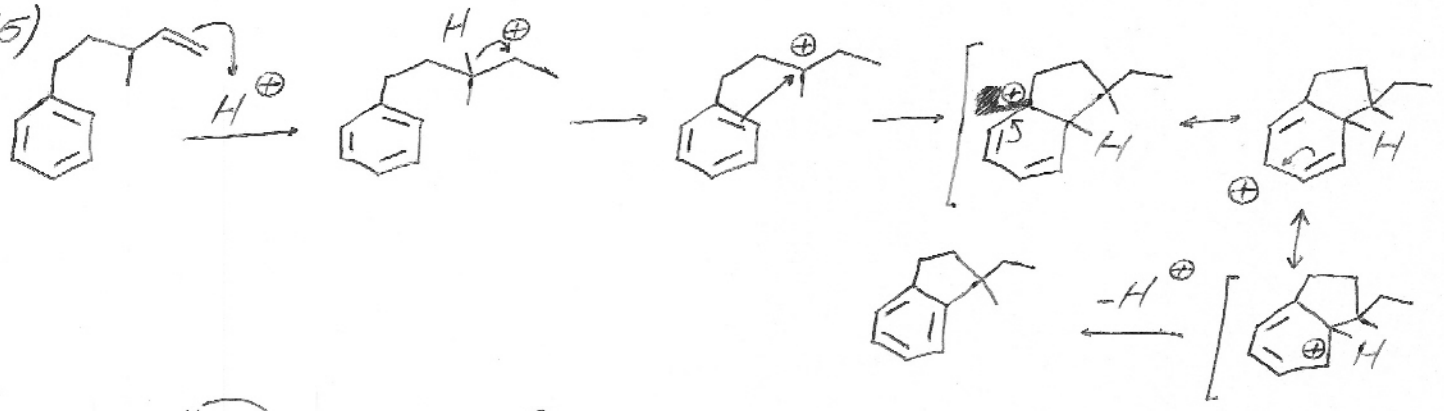
b) 

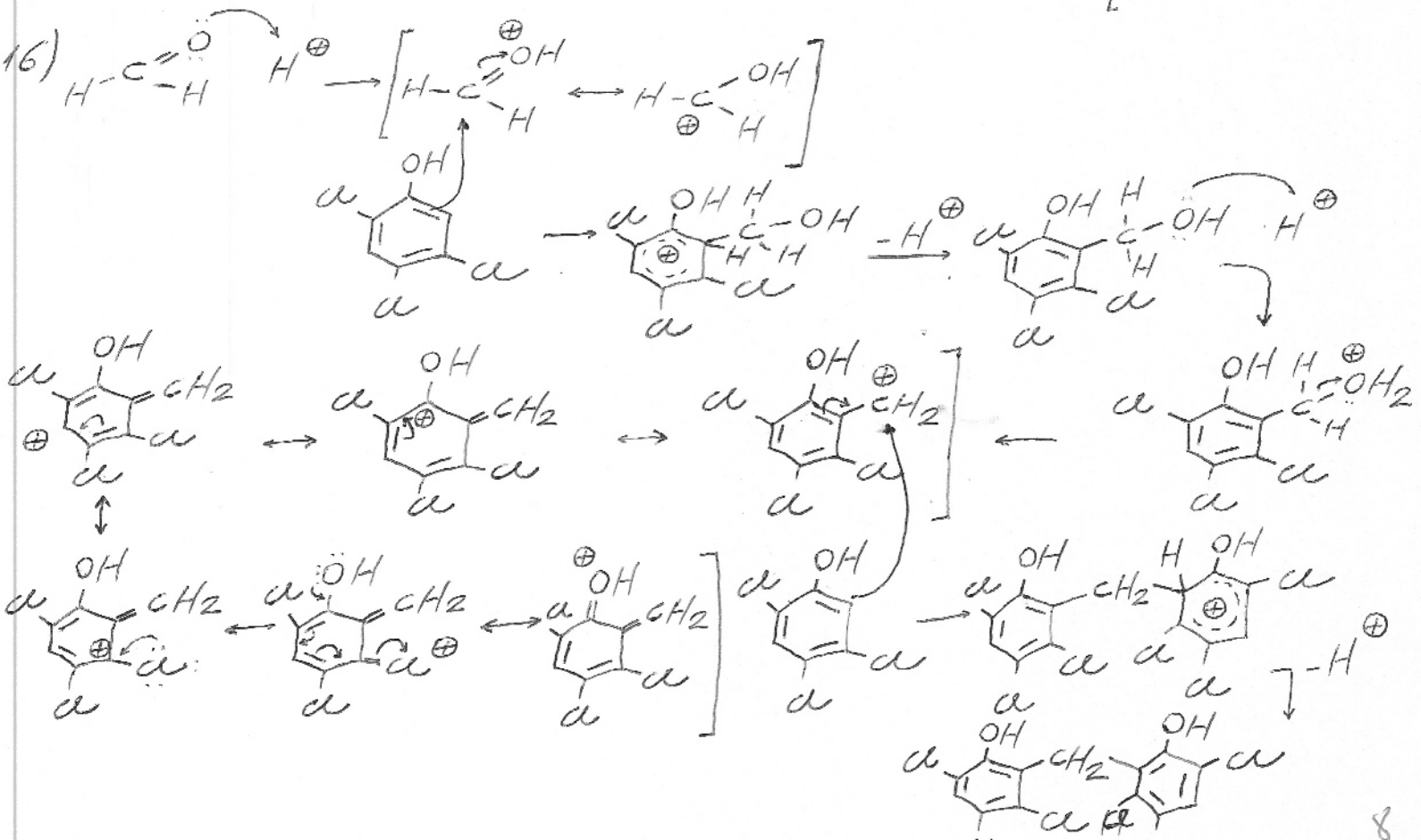
posição para favorecida; menor impedimento estérico; efeito indutivo dos grupos –Cl.

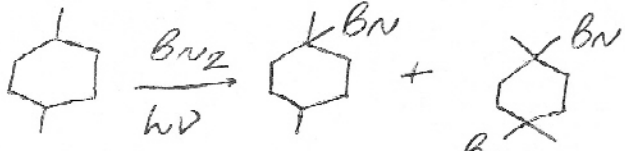
c) 

d) 

orientação definida pelo ativante mais forte ($-OCH_3$).

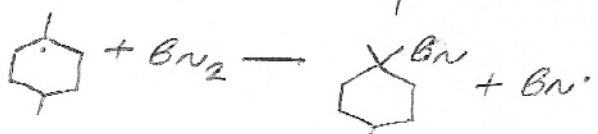
15) 

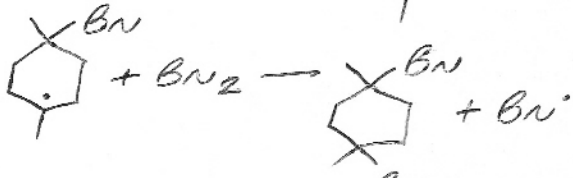
16) 

17)  (os outros possíveis produtos bromados também devem se formar)

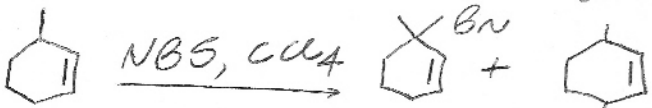
Iniciação: $BrN_2 \xrightarrow{h\nu} 2\,Br\cdot$

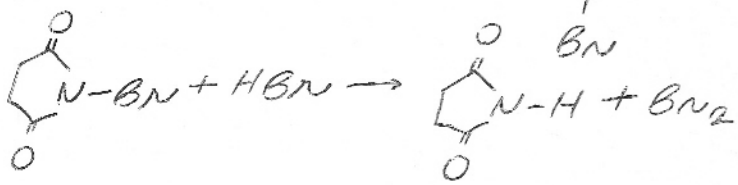
Propagação:





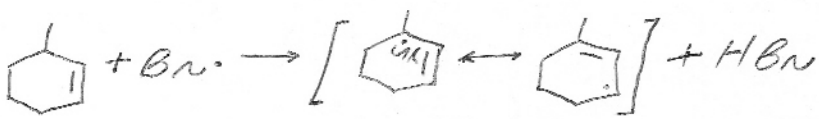
Terminação: Todas as combinações possíveis entre dois radicais

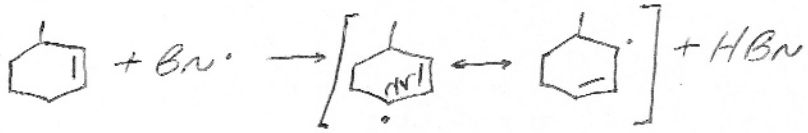


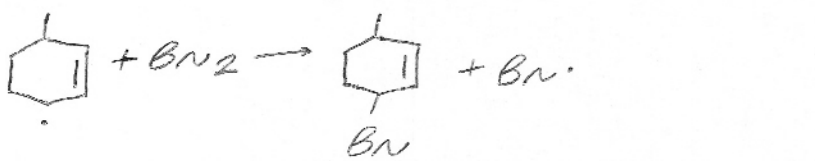


Iniciação: $BrN_2 \rightarrow 2\,Br\cdot$

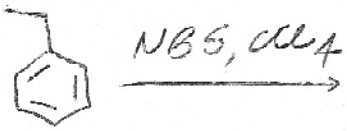
Propagação:





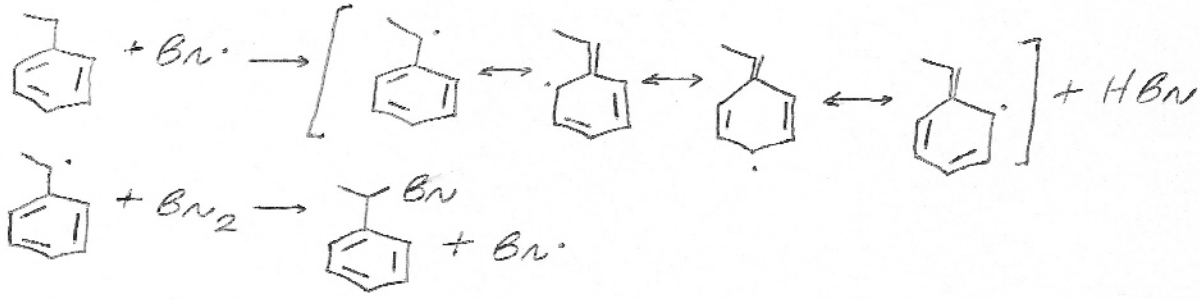


Terminação: combinações possíveis entre dois radicais



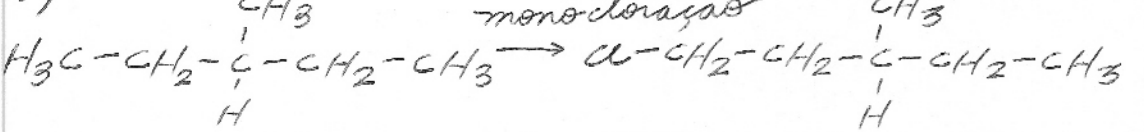
Iniciação: $Br_2 \rightarrow 2\,Br\cdot$

Propagação:

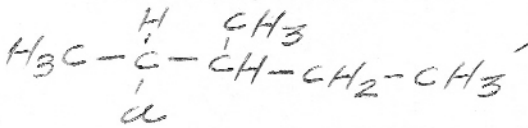


Terminação: combinação entre dois radicais

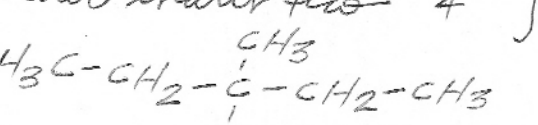
18)



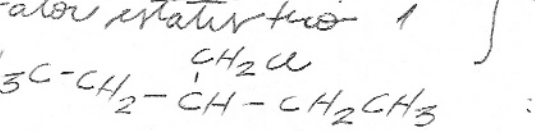
Fator reatividade 1
Fator estatístico 6 } 6



Fator reatividade 3,8
Fator estatístico 4 } 15,2

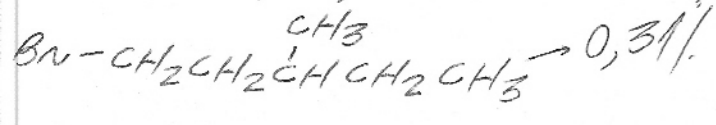


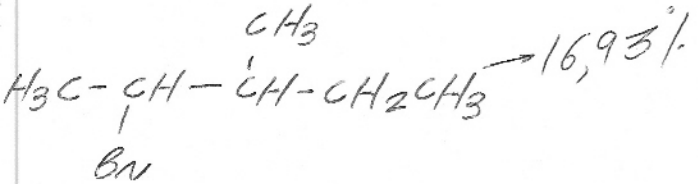
Fator reatividade 5,0
Fator estatístico 1 } 5

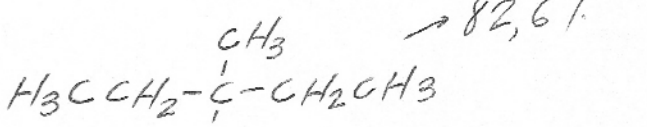


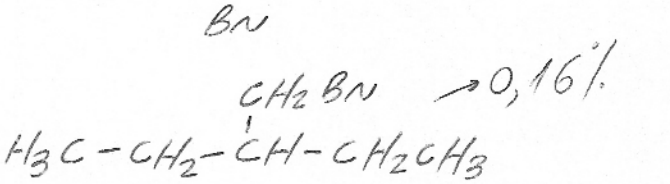
Fator reatividade 1
Fator estatístico 3 } 3

Fazendo o mesmo procedimento para os possíveis produtos de monobromação, temos:

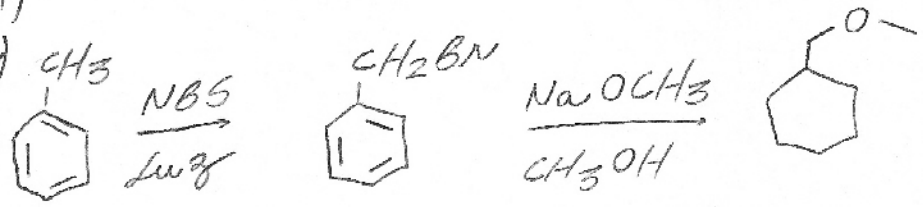


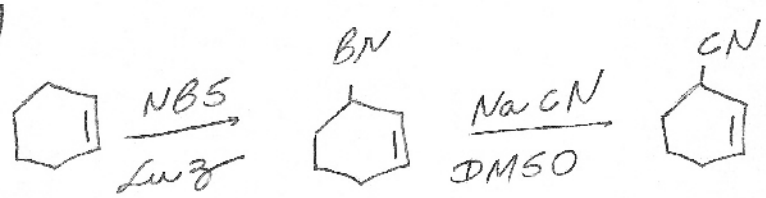




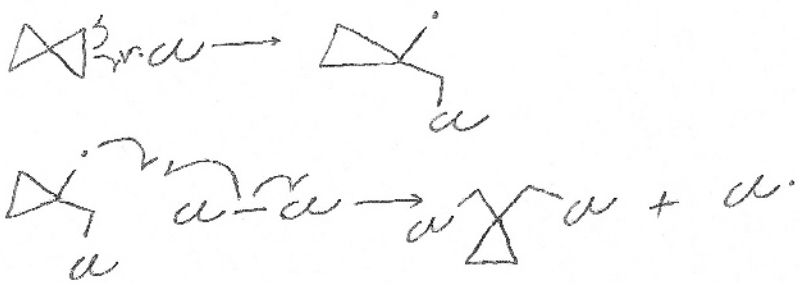


19)

a) 

b) 

20) $Cl_2 \rightarrow 2\,Cl\cdot$



21) $(CH_3)_3C-O\cdot + H_3C-\underset{\underset{H}{|}}{\overset{CH_3}{\overset{|}{C}}}-CH_3 \rightarrow (CH_3)_3C-OH + H_3C-\overset{CH_3}{\overset{|}{\underset{\cdot}{C}}}-CH_3$

terc-butanol

$H_3C-\overset{CH_3}{\overset{|}{\underset{\cdot}{C}}}-CH_3 + Cl-CCl_3 \rightarrow H_3C-\overset{CH_3}{\overset{|}{\underset{Cl}{C}}}-CH_3 + \cdot CCl_3$

cloreto de terc-butila

$H_3C-\overset{CH_3}{\overset{|}{\underset{H}{C}}}-CH_3 + \cdot CCl_3 \rightarrow CHCl_3 + H_3C-\overset{CH_3}{\overset{|}{\underset{\cdot}{C}}}-CH_3$

clorofórmio