Capitolul 5 –EXERCIŢII ŞI PROBLEME PENTRU CONCURSURI
5.3.ALCHINE

Exerciţii şi probleme

5.3. 1. O alchină are densitatea 1,868 în raport cu aerul. **A** conduce la un precipitat roşcat la tratarea cu o soluţie amoniacală de clorură cuproasă. Stabileşte formula structurală a lui **A**.

Rezolvare:

M_{aer} = 28,9 g/mol

M C_nH_{2n-2} = 12n + 2n -2 = (14n -2) g/mol

C_nH_{2n-2}

$d_{aer} = \frac{(14n-2)}{28,9} = 1,868$

14n – 2 = 28,9*1,868

14n – 2 = 54

14n = 56

n = 4

C_4H_{2*4-2} sau C_4H_6 butină care poate fi:

1-butină $HC \equiv C - CH_2 - CH_3$ *sau* 2-butină $H_3C - C \equiv C - CH_3$

Doar 1-butina reacţionează cu $[Cu(NH_3)_2]Cl$ cu formare de precipitat roşu deoarece are legătura triplă marginală şi prezintă un slab caracter acid:

$HC \equiv C - CH_2 - CH_3 + [Cu(NH_3)_2]Cl \rightarrow Cu^{+}\ ^{-}:C \equiv C - CH_2 - CH_3 \downarrow + 2NH_3 + HCl$

$NH_3 + HCl \rightarrow NH_4Cl$

Alchina **A** este 1-butină $HC \equiv C - CH_2 - CH_3$

5.3. 2. La arderea completă a 50 litri dintr-un amestec de propan, etenă şi propină se consumă 190 litri de oxigen şi rezultă 125 litri dioxid de carbon (volumele sunt măsurate în aceleaşi condiţii de temperatură şi presiune). Stabileşte:

a. compoziţia în procente de volum a amestecului de hidrocarburi:
b. considerând apa lichid stabileşte compoziţia în % volum a gazelor de ardere dacă pentru oxidare s-a folosit aer cu 20 % O_2 şi 80 % N_2 (vol).

Rezolvare a:

a + b + c = 100 litri amestec

$\frac{a}{2} + \frac{b}{2} + \frac{c}{2} = 50$ *litri amestec* unde: $\frac{a}{2}$ litri propan, $\frac{b}{2}$ litri etenă şi $\frac{c}{2}$ litri propină

$\frac{a}{2}$ litri		$\frac{5a}{2}$ litri		$\frac{3a}{2}$ litri		
C_3H_8	+	$5O_2$	→	$3CO_2$	+	$4H_2O$
propan		oxigen		dioxid de carbon		apă
22,4 litri		5*22,4 litri		3*22,4 litri		

V_{molar} = 22,4 litri/mol

$\frac{b}{2}$ litri		$\frac{3b}{2}$ litri		$\frac{2b}{2}$ litri		
C_2H_4	+	$3O_2$	→	$2CO_2$	+	$2H_2O$
etenă		oxigen		dioxid de carbon		apă
22,4 litri		3*22,4 litri		2*22,4 litri		

$\frac{c}{2}$ litri		$\frac{4c}{2}$ litri		$\frac{3c}{2}$ litri		
C_3H_4	+	$4O_2$	→	$3CO_2$	+	$2H_2O$
propină		oxigen		dioxid de carbon		apă
22,4 litri		4*22,4 litri		3*22,4 litri		

Amestecul iniţial de gaze:

$\frac{a}{2} + \frac{b}{2} + \frac{c}{2} = 50$

Bilanţul oxigenului:

$\frac{5a}{2} + \frac{3b}{2} + \frac{4c}{2} = 190$ litri O_2

Bilanţul dioxidului de carbon:

$\frac{3a}{2} + \frac{2b}{2} + \frac{3c}{2} = 125$ litri CO_2

a + b + c = 100 (1)

5a + 3b + 4c = 380 (2)

3a + 2b + 3c = 250 (3)

(5a -3a) + (3b -2b) + (4c -3c) = 380 – 250

2a + b + c = 130

a + (a + b + c) = 130

a + 100 = 130

a = 30

b + c = 70 (1)

3*30 + 2b + 3c = 250 (3)

2b + 3c = 160 (3)

2b + 2c + c = 160 (3)

2(b + c) + c = 160

2*70 + c = 160

c = 160 – 140

c = 20

b = 70 – c

b = 70 – 20

b = 50

a + b + c = 100

30 + 50 + 20 = 100

30 % propan, 50 % etenă şi 20 % propină.

Rezolvare b:

100 litri aer……20 litri O_2……80 litri N_2

V_{aer} litri ……190 litri O_2……x litri N_2

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x = 190*80/ 20 = 760 litri N_2

125 litri CO_2

760 + 125 = 885 litri amestec de gaze rezultat

(760 + 125) litri amestec de gaze rezultat……760 litri N_2……125 litri CO_2

100 litri amestec de gaze rezultat……% N_2……% CO_2

% N_2 = 100*760/ 885 = 85,88 % N_2

% CO_2 = 100*125/ 885 = 14,12 % CO_2

5.3. 3. Un amestec gazos **A** este format din propan, propenă şi propină. Prin tratarea a 1 litru de **A** cu clorură cuproasă în soluţie amoniacală rezultă 0,919 g de precipitat. În prezenţa unui exces de brom, 1 litru de **A** (măsurat în condiţii normale) reacţionează cu 4 g de brom. Stabileşte compoziţia în % volum a amestecului.

Rezolvare:

a litri propan C_3H_8

b litri propenă C_3H_6

c litri propină C_3H_4

a + b + c = 1 litru amestec gazos **A**

$$HC \equiv C - CH_3 + [Cu(NH_3)_2]Cl \rightarrow Cu^{+}\ ^{-}:C \equiv C - CH_3 \downarrow + 2NH_3 + HCl$$

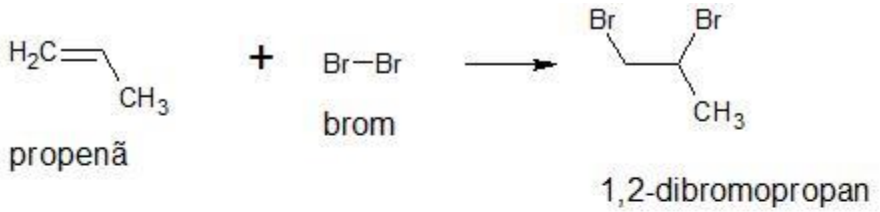
$$NH_3 + HCl \rightarrow NH_4Cl$$

c litri				0,919 g				
$HC \equiv C - CH_3$	+	$[Cu(NH_3)_2]Cl$	→	$Cu^{+}\ ^{-}:C \equiv C - CH_3 \downarrow$	+	NH_3	+	NH_4Cl
propină		clorură diamino Cu(I)		precipitat roşu		amon iac		clorură de amoniu
22,4 litri				103 g				

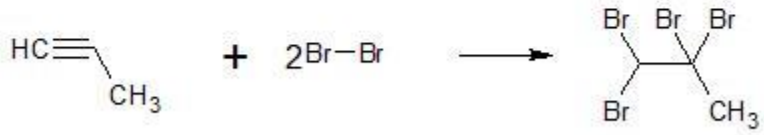
V_{molar} = 22,4 litri/mol

M CH_3 -C≡C:$^-$ Cu^+ = 3*12 + 3 + 64 = 39 + 64 = 103 g/mol

c = 22,4*0,919/ 103 = 0,2 litri propină



propenă 1,2-dibromopropan



propină 1,1,2,2-tetrabromopropan

c = 0,2 litri		x g		
HC ≡ C – CH_3	+	$2Br_2$	→	$Br_2HC – CBr_2-CH_3$
propină		brom		1,1,2,2-tetrabromopropan
22,4 litri		2*160 g		

V_{molar} = 22,4 litri/mol

M Br_2 = 160 g/mol

x = 0,2*2*160/ 22,4 = 64/ 22,4 = 2,86 g Br_2

b litri		y = 1,14 g		
H_2C = CH – CH_3	+	Br_2	→	$BrH_2C – CHBr-CH_3$
propenă		brom		1,2-dibromopropan
22,4 litri		160 g		

V_{molar} = 22,4 litri/mol

x + y = 4 g Br_2

y = 4 -2,86 = 1,14 g Br_2 se adiţionează la propenă

b = 22,4*1,14/ 160 = 0,1596 litri propenă

TOTAL	C_3H_8	C_3H_6	C_3H_4
	propan	propenă	propină
1 litru	a = 0,64 litri	b = 0,1596 litri	c = 0,2 litri

a + b + c = 1

a = 1 – 0,1596 – 0,2

a = 0,64 litri propan C_3H_8

1 litru amestec……..0,64 litri propan…….0,1596 litri propenă……..0,2 litri propină

100 litri amestec……% propan……% propenă…….% propină

% propan = 64 % C_3H_8

% propenă = 15,96 % C_3H_6

% propină = 20 % C_3H_4

5.3. 4. Un compus **A** (C_6H_{10}) conduce la n-hexan prin hidrogenare totală. Tratat cu o soluţie acidă de sulfat mercuric **A** conduce la **B** ($C_6H_{12}O$). Oxidarea energică a lui **A** conduce numai la acid propanoic (CH_3-CH_2-COOH). Stabileşte formula structurală probabilă pentru **A**.

Rezolvare:

Compus **A** : C_6H_{10} → n-hexan C_6H_{2*6+2} adică C_6H_{14}

$C_6H_{10} + 2H_2 \rightarrow C_6H_{14}$

Catenă liniară $H_3C – CH_2 – CH_2 – CH_2 – CH_2 – CH_3$ n-hexan

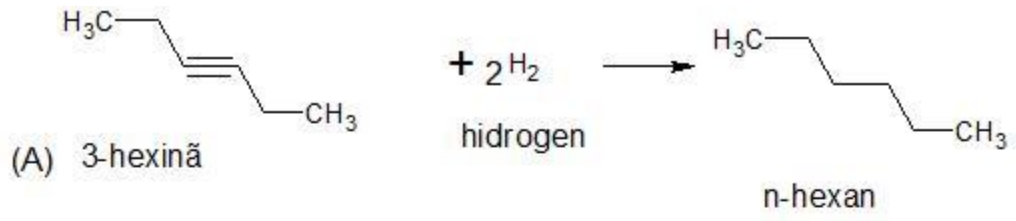
Compusul A (C_6H_{10}) are catenă liniară şi este o alchină deoarece reacţionează cu o soluţie acidă de sulfat mercuric şi se obţine **B** ($C_6H_{12}O$) :

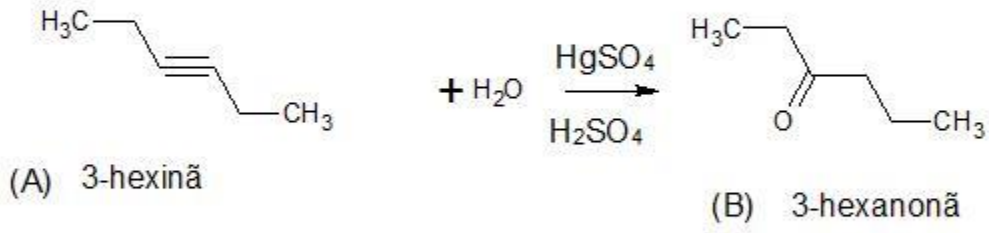
C_6H_{10}	+	H_2O	→	$C_6H_{12}O$
A		apă	$HgSO_4 + H_2SO_4$	**B**

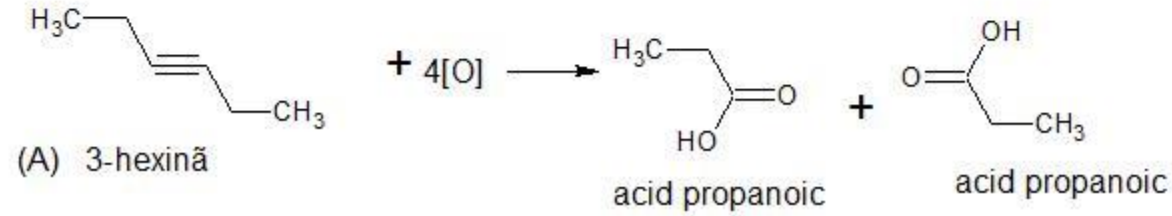
$H_3C–CH_2–COOH + HOOC–CH_2-CH_3 \leftarrow 4[O] + H_3C–CH_2–C \equiv C–CH_2–CH_3$

$H_3C–CH_2–C \equiv C–CH_2–CH_3$	+	4[O]	→	$2H_3C–CH_2–COOH$
3-hexină **(A)**				acid propanoic

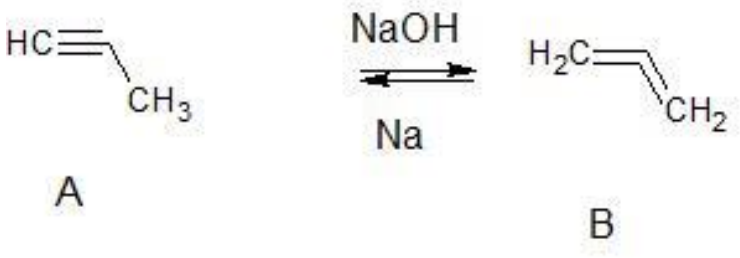
$H_3C–CH_2–C \equiv C–CH_2–CH_3$	+	H_2O	→	$H_3C–CH_2–CO-CH_2–CH_2–CH_3$
3-hexină **(A)**			Kucerov	3-hexanonă (B)



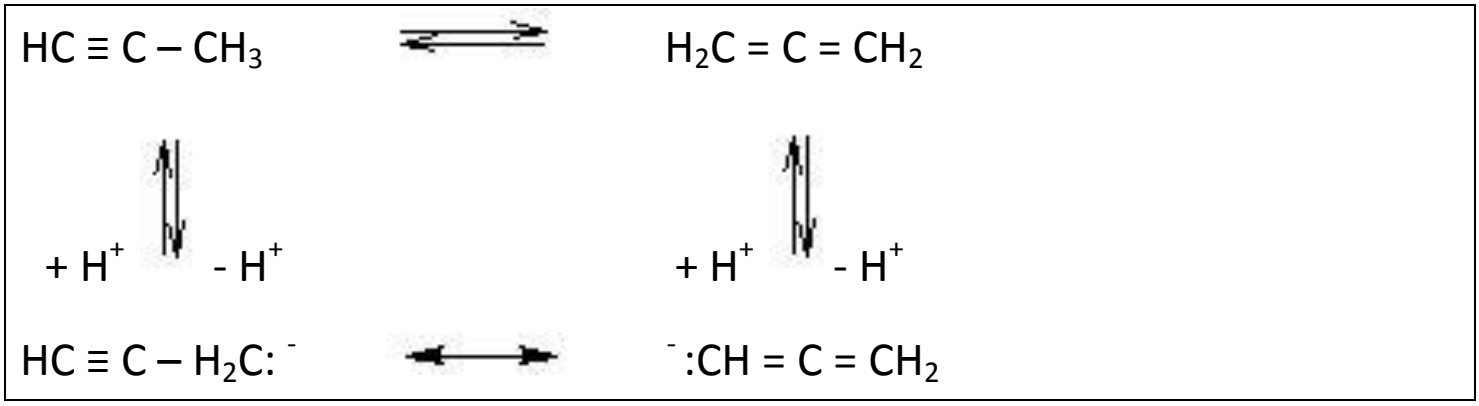




5.3. 5. Se dă reacţia:



Examinând cele două structuri se constată că **A** (alchina) este tautomeră cu **B** (alena).
Tautomeria de mai sus se realizează conform echilibrelor:



Stabileşte:

a. masa de amidură de sodiu ($NaNH_2$) cu care pot reacţiona 5,6 ml de propină (c.n.);
b. masa de $NaOH$ cu care poate reacţiona acelaşi volum de propină;
c. formulele celor doi produşi de reacţie.

Rezolvare:

1 mol propină reacţionează cu 1 mol $NaNH_2$

V_{molar} = 22,4 litri/mol

$M\ NaNH_2$ = 23 +14 + 2 = 39 g/mol

22,4 litri propină……1 mol propină

$5,6 * 10^{-3}$ litri propină……..n moli propină

$n = 5,6*10^{-3}/22,4 = 0,25*10^{-3}$ moli propină

m $NaNH_2 = 0,25*39*10^{-3}$ = 9,75 mg amidură de sodiu

1 mol propină reacţionează cu 1 mol NaOH

M NaOH = 23 +16 + 1 = 40 g/mol

m NaOH = $0,25*40*10^{-3}$ = 10 mg hidroxid de sodiu

$HC \equiv C - H_2C:^-$ ⟷ $^-:CH = C = CH_2$

$[HC \equiv C = CH_2]^- Na^+$

5.3. 6. Stabiliţi formulele compuşilor finali obţinuţi prin fiecare din următoarele succesiuni de reacţie:

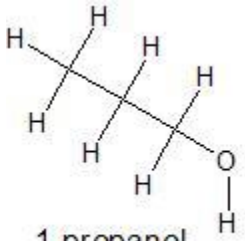
a.	- H_2O		Br_2		KOH		$NaNH_2$	
$H_3C-CH_2-CH_2-OH$	⟶	A	⟶	B	⟶	C	⟶	D
	H_3O^+				alc.			

b.	Br_2		KOH		$[Cu(NH_3)_2]Cl$	
etena	⟶	A	⟶	B	⟶	C
			alc.		2 moli	

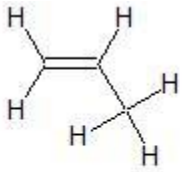
c.	Br_2		KOH		H_2O			
propena	⟶	A	⟶	B	⟶	C	⟷	D
			alc.		$HgSO_4$			

d.	PCl_5		KOH		Na		CH_3-I	
H_3C- CH_2- HC=O	—→	A	—→	B	—→	C	—→	D
			alc.					

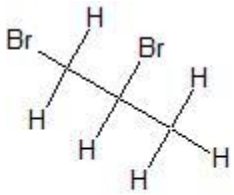
Rezolvare:



1-propanol



propenã



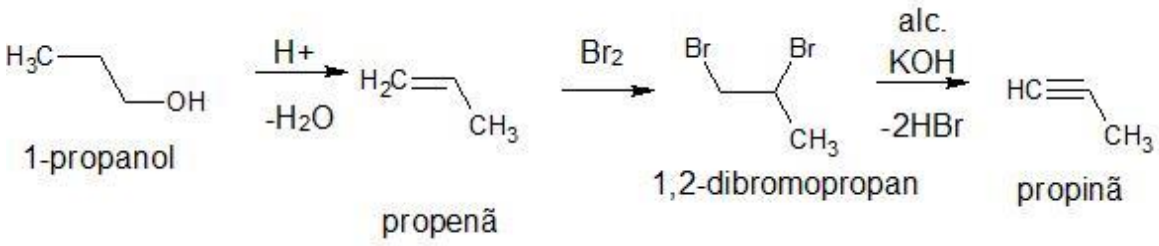
1,2-dibromopropan

a.		A		
H_3C -CH_2 -CH_2 -OH	→	H_3C –HC = CH_2	+	H_2O
1-propanol	H_3O^+	propenă		apă

A				B
H_3C –HC = CH_2	+	Br_2	→	H_3C –BrCH - CH_2Br
propenă		brom		1,2-dibromopropan

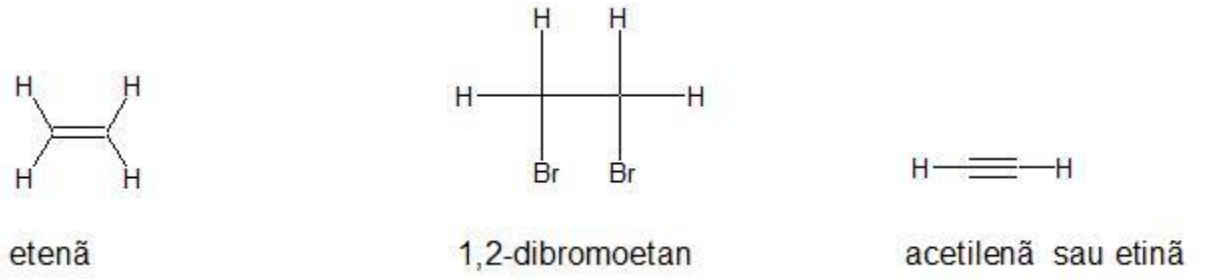
B	KOH	C		
H_3C –BrCH - CH_2Br	→	H_3C –C ≡ CH	+	2HBr
1,2-dibromopropan	alc.	propină		acid bromhidric

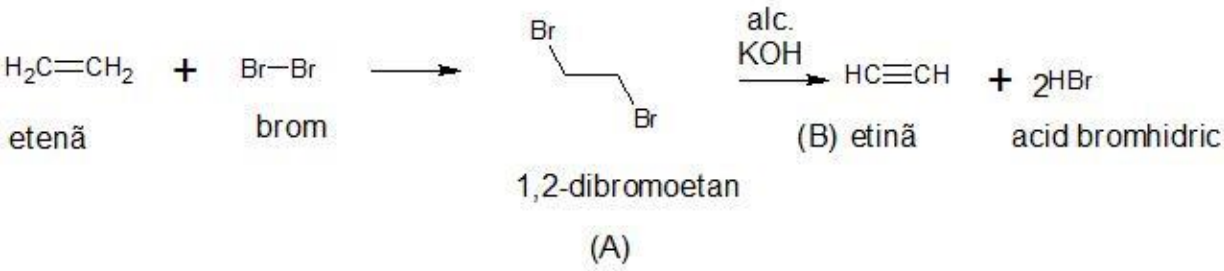
C				D
H_3C –C ≡ CH	+	$NaNH_2$	→	H_3C –C ≡ $C:^-$ Na^+
propină			-NH_3	



$H_3C – C \equiv CH + NaNH_2 \rightarrow H_3C – C \equiv C:^- Na^+ + NH_3$

Rezolvare b:





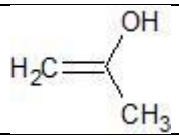
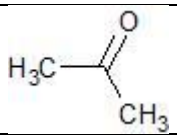
$HC \equiv CH + 2[Cu(NH_3)_2]Cl \rightarrow Cu^+ {}^-:C \equiv C:^- Cu^+ \downarrow + 2NH_4Cl + 2NH_3$

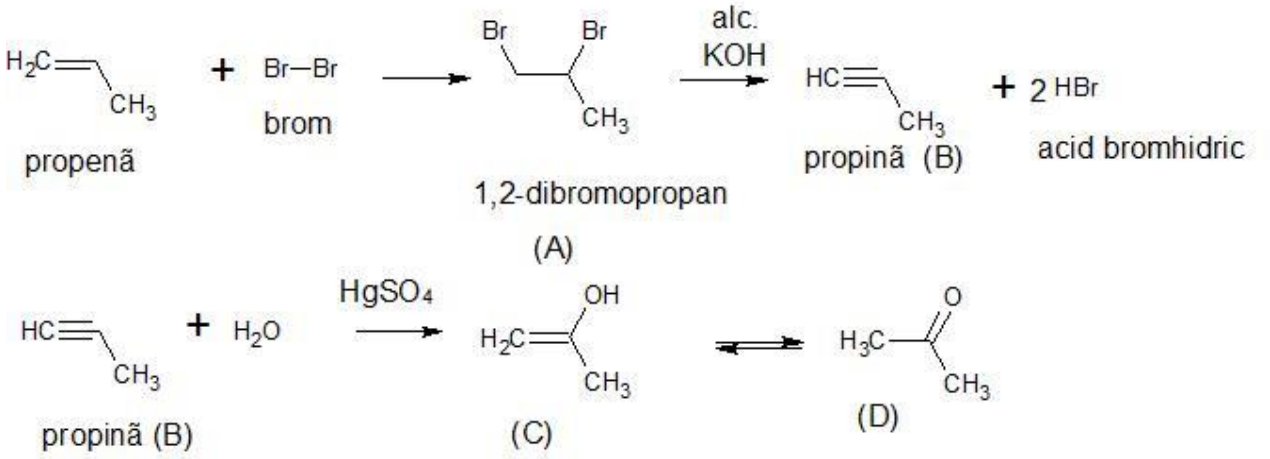
C este $Cu^+ {}^-:C \equiv C:^- Cu^+ \downarrow$ precipitat roşu

A este $Br – CH_2 – CH_2 – Br$ 1,2-dibromoetan, iar B este $HC \equiv CH$ etina sau acetilenă

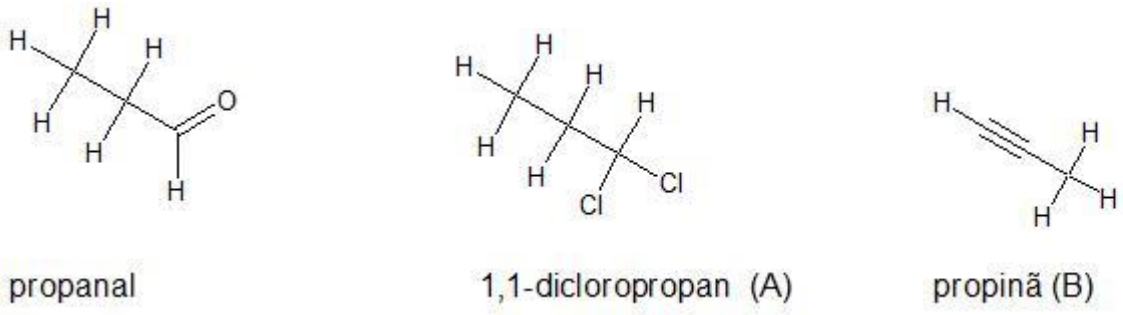
C.				A
$H_3C – HC = CH_2$	+	Br_2	→	$H_3C – BrCH - CH_2Br$
propenă		brom		1,2-dibromopropan

A	KOH	B		
H_3C –BrCH - CH_2Br	→	H_3C –C ≡ CH	+	2HBr
1,2-dibromopropan	alc.	propină		acid bromhidric

B	H_2O	C		D
H_3C –C ≡ CH	→		⇌	
propină	$HgSO_4$	enol		propanonă

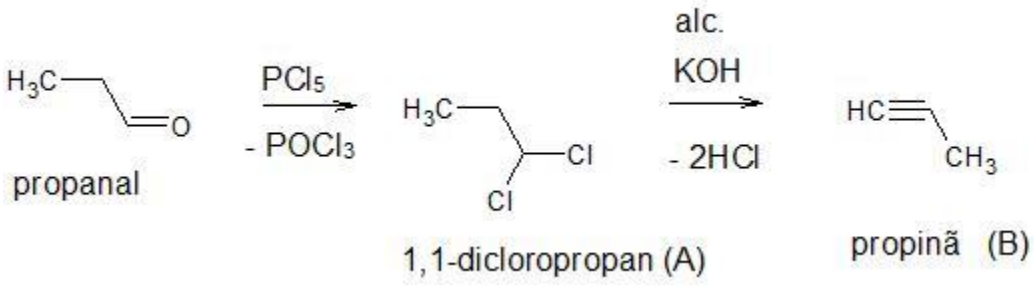


Rezolvare d:



H_3C –CH_2 -HC = O + PCl_5 → H_3C –CH_2 –$HCCl_2$ + $POCl_3$

H_3C –CH_2 –$HCCl_2$ → H_3C – C ≡ CH + 2HCl



$H_3C–C \equiv CH + Na \rightarrow H_3C–C \equiv C:^- Na^+ + 1/2H_2$

$H_3C–C \equiv C:^- Na^+ + CH_3\text{-}I \rightarrow H_3C–C \equiv C–CH_3 + NaI$

C este $H_3C–C \equiv C:^- Na^+$

D este $H_3C–C \equiv C–CH_3$ 2-butină

5.3. 7. Se dispune de toţi compuşii anorganici necesari şi de acetilenă şi iodură de metil ca singuri reactanţi organici. Indică etapele sintezei compuşilor următori pornind de la materiile prime menţionate anterior.

a. propină;
b. 2-butină;
c. trans-2-butenă;
d. $H_3C–CH_2–CBr_2–HCBr_2$;
e. $H_3C\text{-}CH_2\text{-}HC=O$
f. $H_2C = CH–COOH$;
g. $H_3C–CBr_2–CH_3$.

Rezolvare a:

$HC \equiv CH + Na \rightarrow HC \equiv C:^- Na^+ + 1/2H_2 \uparrow$

$HC \equiv C:^- Na^+ + CH_3–I \rightarrow HC \equiv C–CH_3 + NaI$

Rezolvare b:

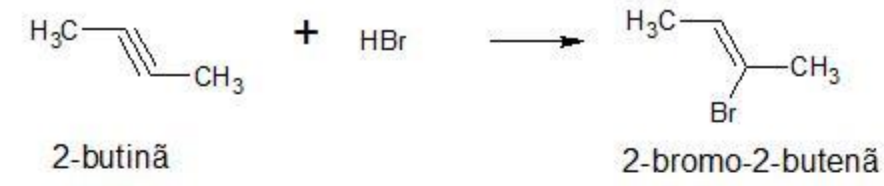
$HC \equiv CH + 2Na \rightarrow Na^+ \ ^-:C \equiv C:^- Na^+ + H_2 \uparrow$

$Na^+ \ ^-:C \equiv C:^- Na^+ + 2CH_3–I \rightarrow H_3C- C \equiv C –CH_3 + 2NaI$

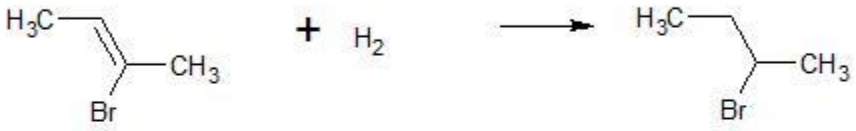
Rezolvare c:

$HC \equiv CH + 2Na \rightarrow Na^+ \ ^-:C \equiv C:^- Na^+ + H_2 \uparrow$

$Na^+ \ ^-:C \equiv C:^- Na^+ + 2CH_3–I \rightarrow H_3C- C \equiv C –CH_3 + 2NaI$

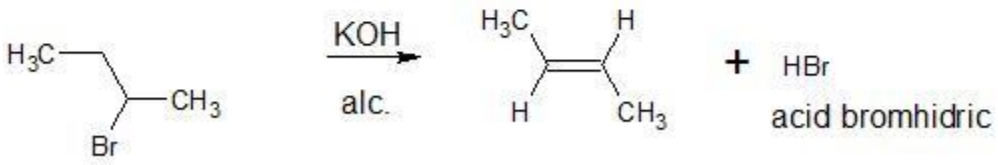


2-butinã 2-bromo-2-butenã



2-bromo-butan

2-bromo-2-butenã



acid bromhidric

2-bromobutan trans-2-butenã

$H_3C- C \equiv C –CH_3 + HBr \rightarrow H_3C- HC = CBr –CH_3$

$H_3C- HC = CBr –CH_3 + H_2 \rightarrow H_3C- H_2C - CHBr –CH_3$

În prezenţă de KOH alc.:

H_3C- H_2C - CHBr –CH_3 → trans 2-butenă H_3C –HC = CH –CH_3 + HBr

Rezolvare d:

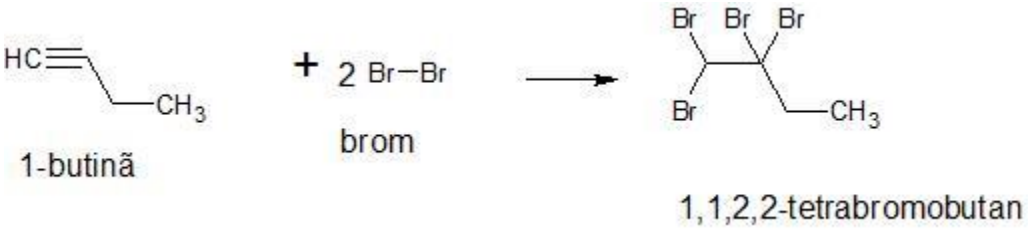
$HC \equiv CH + Na \rightarrow HC \equiv C:^- Na^+ + 1/2H_2 \uparrow$

$HC \equiv CH + H_2 \rightarrow H_2C = CH_2$ (în prezenţă de Pd/Pb^{2+})

$H_2C = CH_2 + HI \rightarrow CH_3\text{-}CH_2\text{-}I$

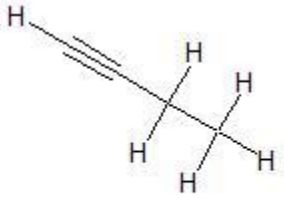
$HC \equiv C:^- Na^+ + CH_3\text{-}CH_2 – I \rightarrow HC \equiv C – CH_2 – CH_3 + NaI$

$HC \equiv C – CH_2 – CH_3 + 2Br_2 \rightarrow Br_2HC – CBr_2 – CH_2 – CH_3$

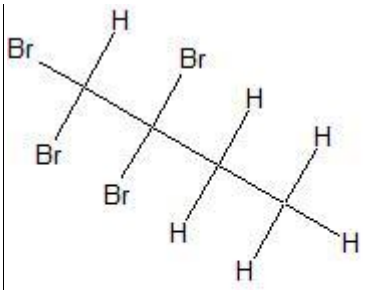


1-butină

1,1,2,2-tetrabromobutan



1-butină



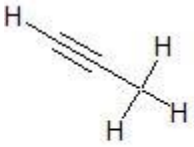
1,1,2,2-tetrabromobutan

Rezolvare e:

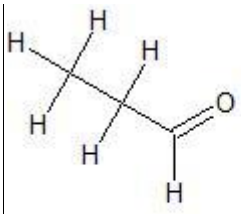
$HC \equiv CH + Na \rightarrow HC \equiv C:^- Na^+ + 1/2H_2 \uparrow$

$HC \equiv C:^- Na^+ + CH_3 – I \rightarrow HC \equiv C – CH_3 + NaI$

$HC \equiv C - CH_3$	+	H_2O	→	$H_3C - CH_2 - HC = O$
propină		apă	B_2H_6	propanal
			H_2O_2	



propinã

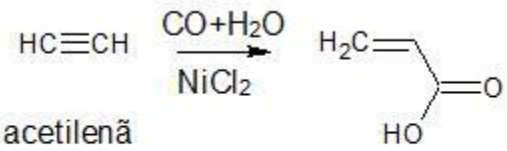


propanal

Rezolvare f:

În prezenţă de $NiCl_2$:

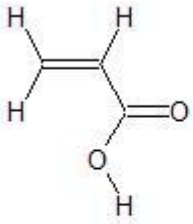
$$HC \equiv CH + CO + H_2O \rightarrow H_2C = CH - COOH$$



acetilenã

acid acrilic

acetilenã sau etinã



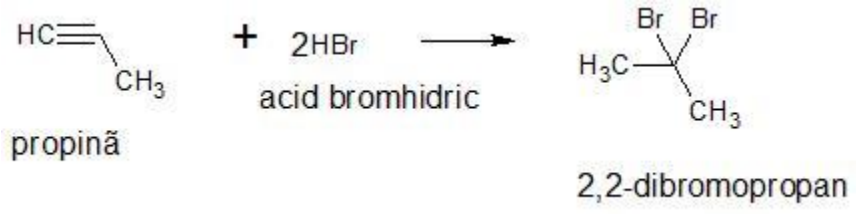
acid acrilic

Rezolvare g:

$HC \equiv CH + Na \rightarrow HC \equiv C:^- Na^+ + 1/2H_2 \uparrow$

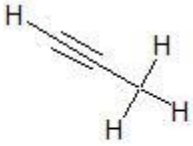
$HC \equiv C:^- Na^+ + CH_3–I \rightarrow HC \equiv C–CH_3 + NaI$

$HC \equiv C–CH_3 + 2H\text{-}Br \rightarrow H_3C–CBr_2–CH_3$

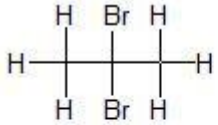


propinã

2,2-dibromopropan



propinã



2,2-dibromopropan

5.3. 8. O alchină **A** reacţionează cu sodiu metalic. **A** conţine 88,9 % C şi reacţionează cu acidul sulfuric diluat în prezenţă de sulfat mercuric conducând la **B**. Prin reducerea lui **B** se obţine **D** care prin încălzire cu acid sulfuric concentrat conduce la un amestec de trei hidrocarburi izomere **E, F, G**. **E** şi **F** sunt izomeri geometrici iar **G** poate fi obţinută direct din A printr-o reacţie ce are loc în prezenţa paladiului dezactivat. Stabileşte formulele de structură probabile pentru fiecare din compuşii **A, B, D, E, F ,G.**

Rezolvare:

C_nH_{2n-2}

$M\ C_nH_{2n-2} = 12n + 2n - 2 = (14n - 2)$ g/mol

(14n – 2) g alchină……12n g C

100 g alchină……88,9 g C

88,9*(14n – 2) = 12n*100

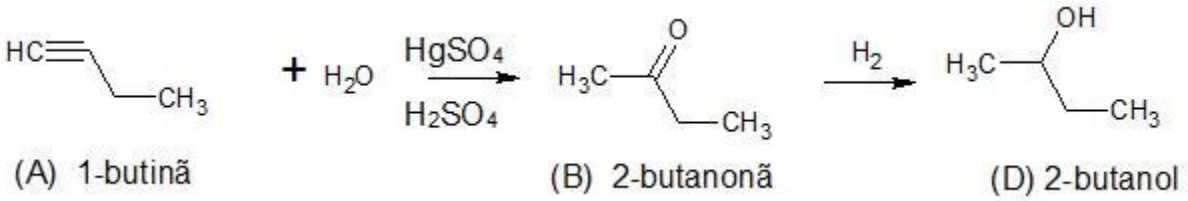
14n*88,9 – 1200n = 2*88,9

n*(1244,6 – 1200) = 177,8

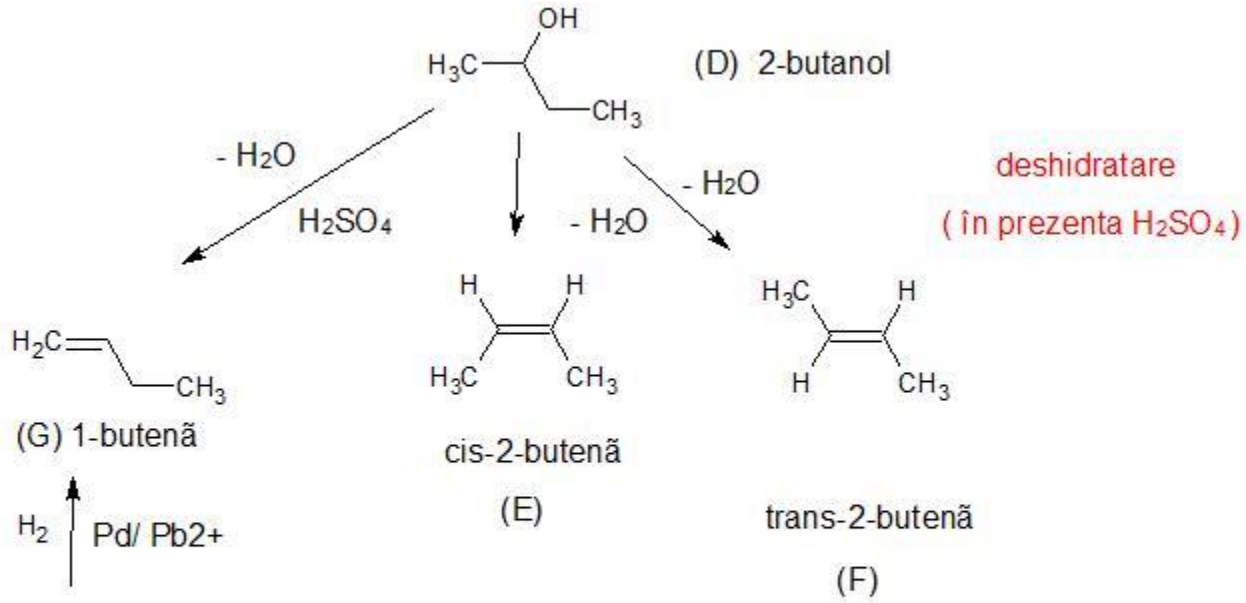
n = 177,8/ 44,6

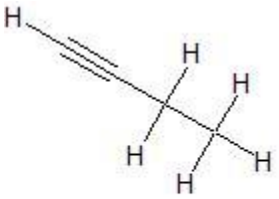
n = 4

C_4H_6 alchina $HC \equiv C - CH_2 - CH_3$ 1-butină

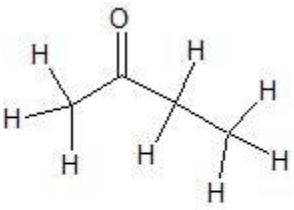


(A) 1-butină (B) 2-butanonă (D) 2-butanol

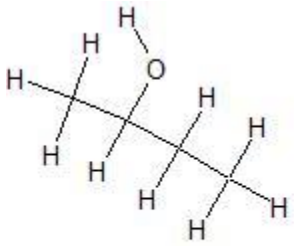




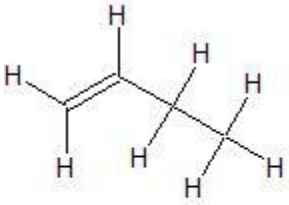
(A) 1-butinã



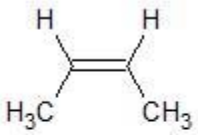
(B) 2-butanonã



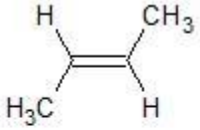
(D) 2-butanol



(G) 1-butenã



(E) cis-2-butenã



(F) trans-2-butenã