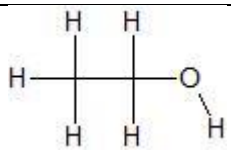
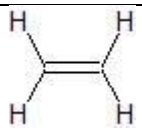
Capitolul 5 –EXERCIŢII ŞI PROBLEME PENTRU CONCURSURI
5.6.ACIZI CARBOXILICI

Exerciţii şi probleme

5.6. 1. Stabileşte formulele structurale ale compuşilor notaţi cu litere în transformările de mai jos:

a	 alcool etilic	PI_3		KCN		H_2O			
		→	A	→	B	→	C		
						H_3O^+			

b	 etenă	Br_2		KCN		H_2O		C_2H_5OH	
		→	A	→	B	→	C	→	D
				(2 echiv.)		H_3O^+		(2 echiv.)	

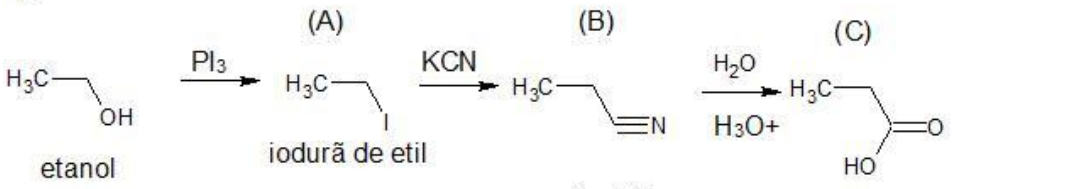
c	H – C ≡ C – H acetilenă	H_2O		[O]		$CaCO_3$			
		→	A	→	B	→	C	→	D
		$HgSO_4$		$KMnO_4/H_3O^+$				t^0C	

d	HC ≡ C – CH_3 propină	$NaNH_2$		1.CO_2		H_2	
		→	A	→	B	→	C
		$-NH_3$		2.H_2O		Pd/Pb^{2+}	

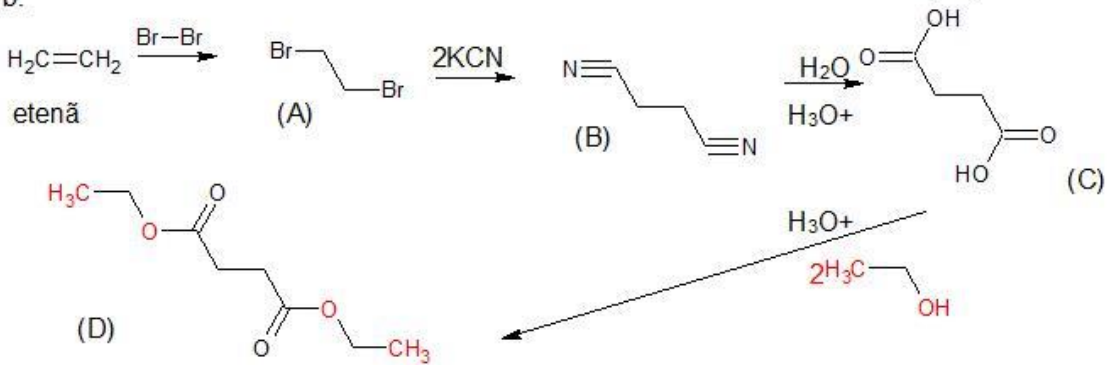
e	 benzen	CH_3-Cl		[O]		PCl_5		C_2H_5OH	
		→	A	→	B	→	C	→	D
		$AlCl_3$		$KMnO_4/H_3O^+$				H_3O^+	

Rezolvare:

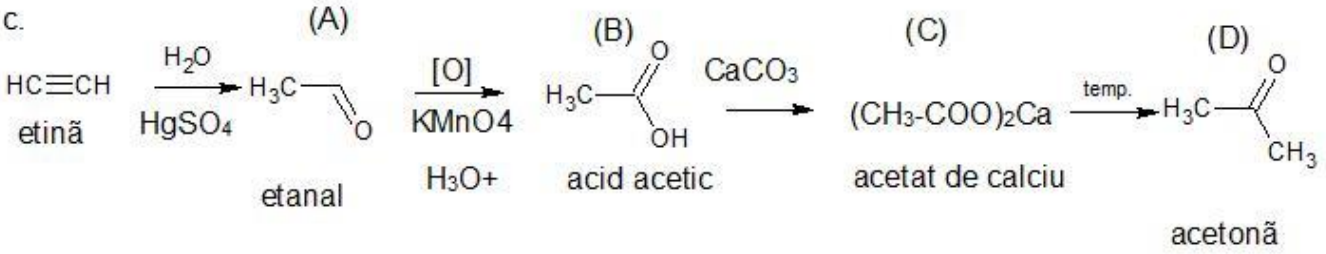
a.



b.

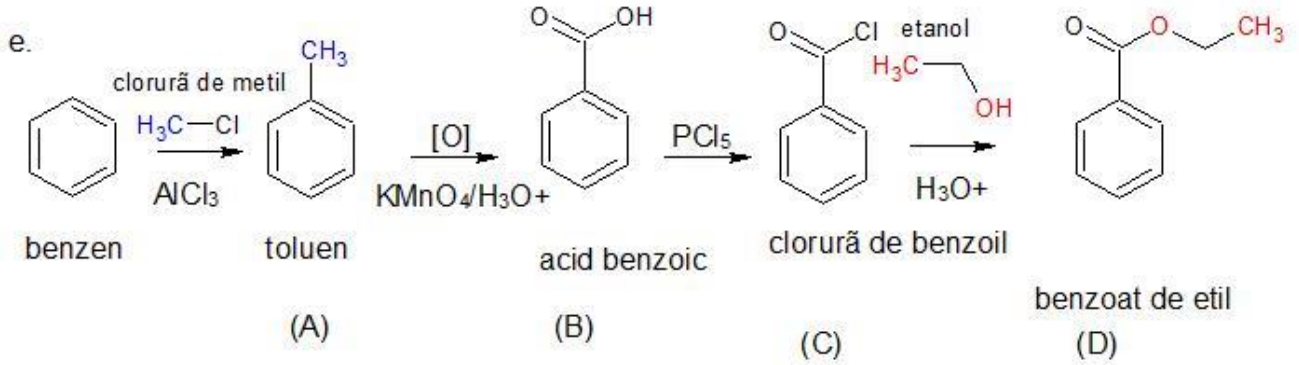


c.



d	HC ≡ C – CH_3 propinã	$NaNH_2$		1.CO_2		H_2	
		→	Na^{+-}:C≡C-CH_3	→	HOOC-C≡C-CH_3	→	HOOC-HC=CH-CH_3
		-NH_3	**A**	2.H_2O	**B**	Pd/Pb^{2+}	**C**

e.



5.6. 2. Stabileşte formulele structurale ale compuşilor notaţi cu litere în transformările de mai jos:

a		H_2O		$CH_2(COOH)_2$			
	A	⟶	B	⟶	C	⟶	acid crotonic
		$HgSO_4$				t^0C	

b		HBr		$NaCH(COOC_2H_5)_2$		H_2O			
	A	⟶	B	⟶	C	⟶	D	⟶	acid butanoic
						H_3O^+		t^0C	

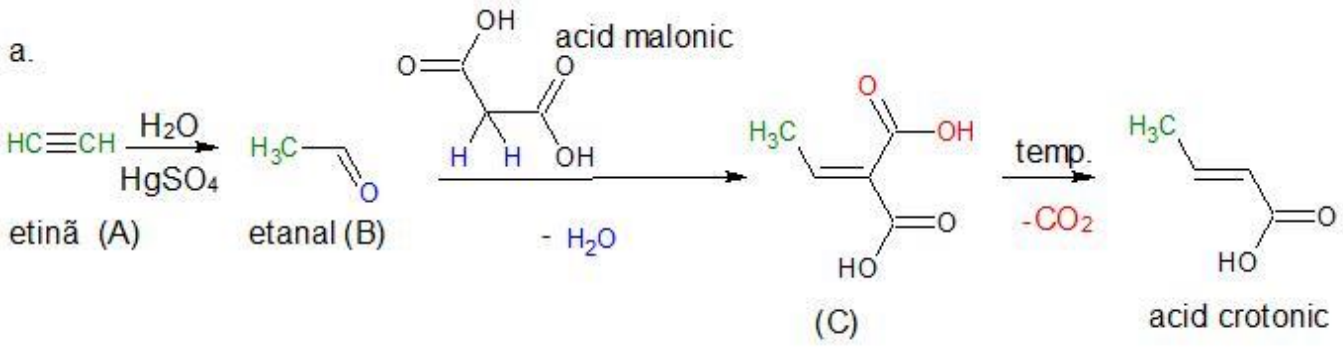
c		[O] 2 etape		Cl_2		KCN		H_2O	
	A	⟶	B	⟶	C	⟶	D	⟶	acid malonic
		$KMnO_4/H_3O^+$		(1 echiv.)					

d		PBr_3		Mg		$1.CO_2$		PCl_5		$1.CH_2N_2$	
	A	⟶	B	⟶	C	⟶	D	⟶	E	⟶	acid butanoic
				eter		$2.H_2O/H_3O+$				$2.H_2O$	

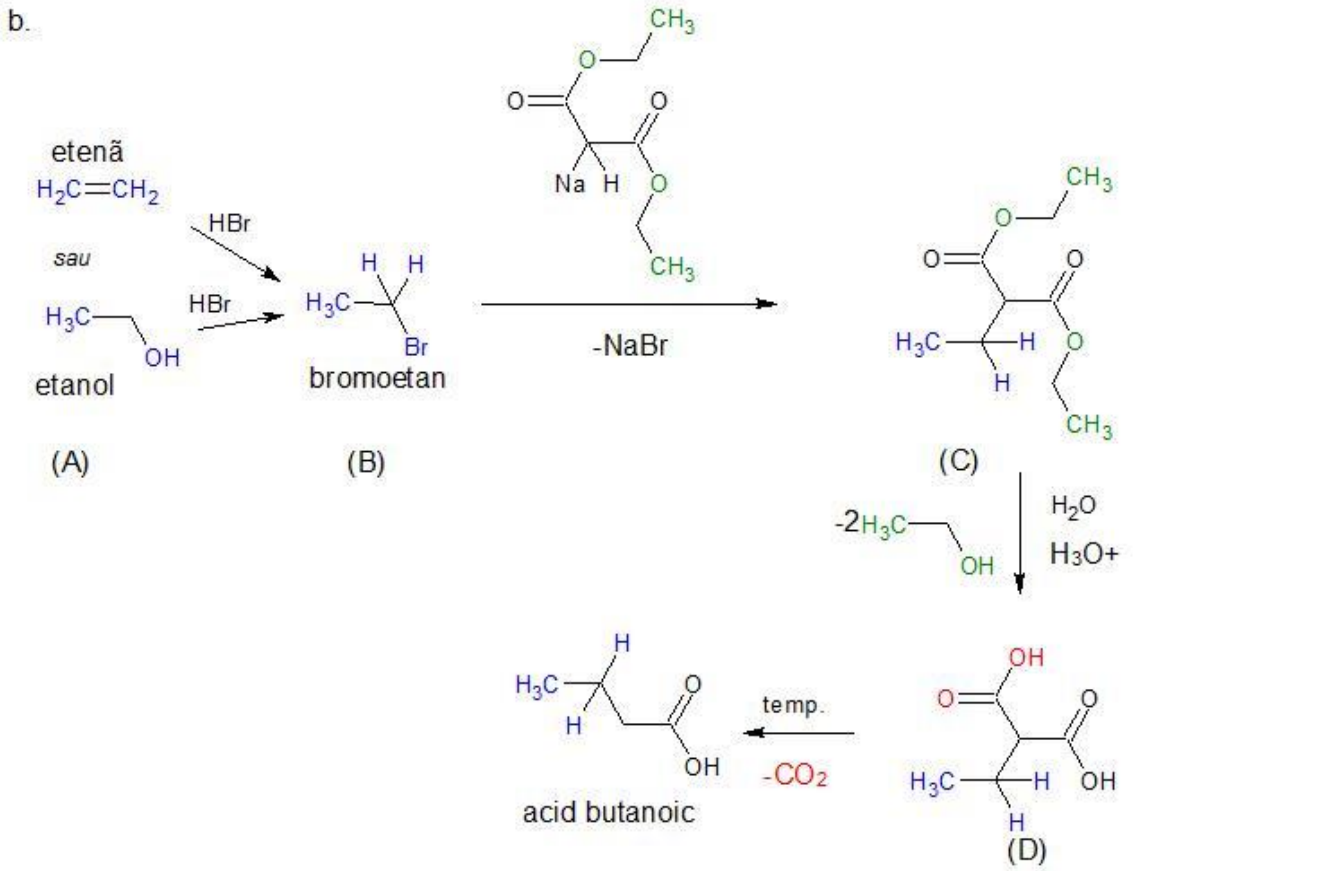
e		red.		Diazotare		CuCN		H_2O			
	A	⟶	B	⟶	C	⟶	D	⟶	E	⟶	acid p-toluic
		Fe + HCl						H_3O^+			

Rezolvare:

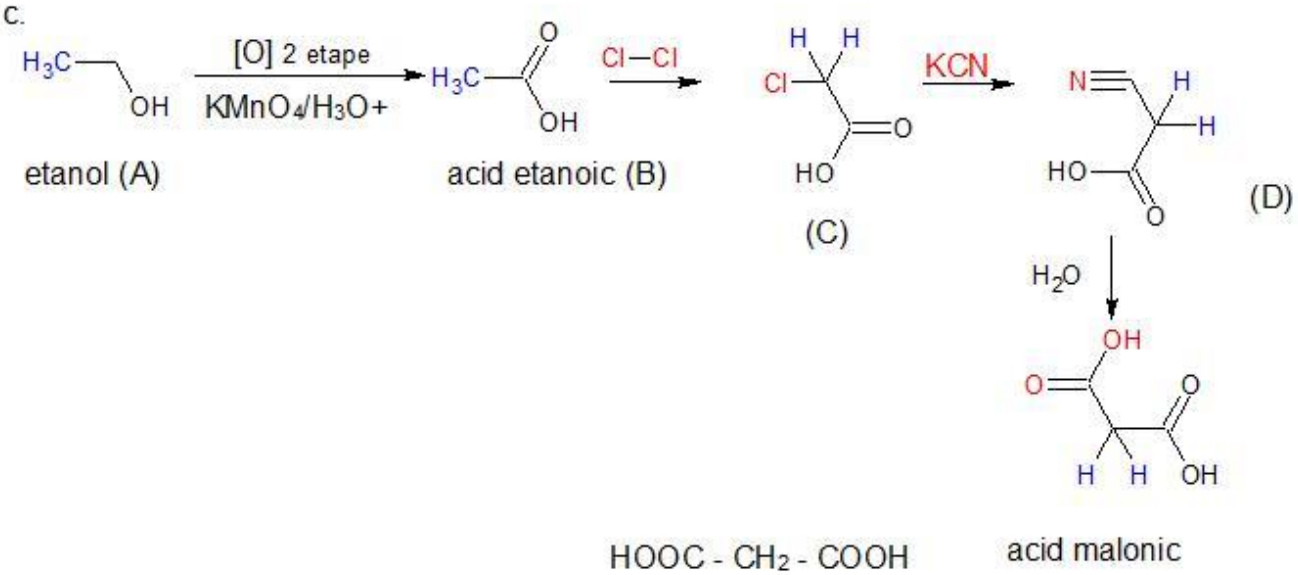
a.



b.



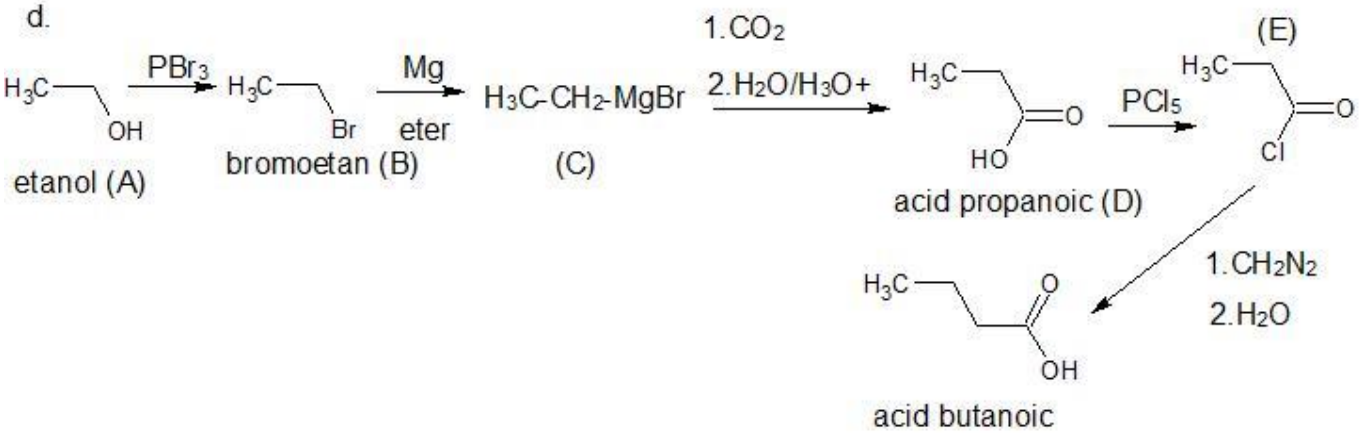
c.



etanol (A) acid etanoic (B) (C)

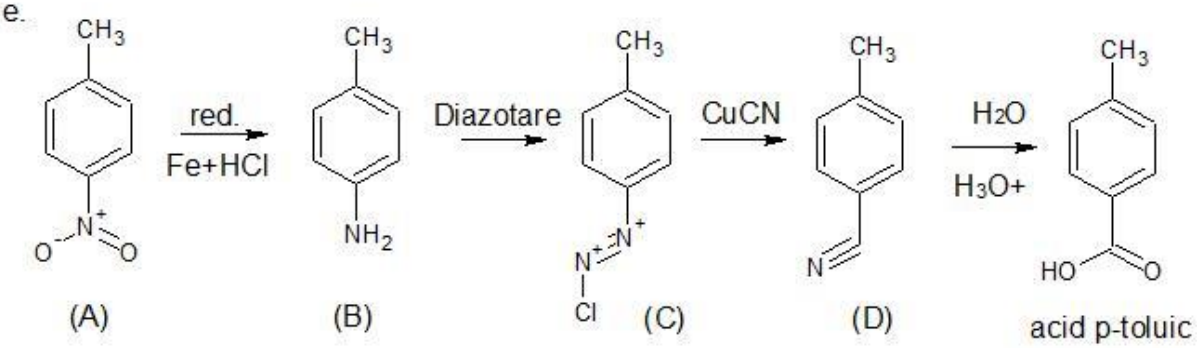
$HOOC - CH_2 - COOH$ acid malonic

d.



etanol (A) bromoetan (B) (C) acid propanoic (D) acid butanoic

e.



(A) (B) (C) (D) acid p-toluic

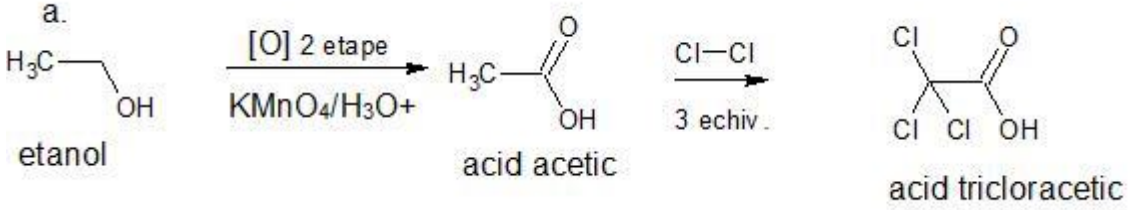
(C) $H_3C - C_6H_4 - N \equiv N^+Cl^-$

5.6. 3. Pornind de la alcool etilic ca singur compus organic, utilizând toţi reactivii anorganici necesari, concepe câte o alternativă de sinteză pentru fiecare din compuşii următori:

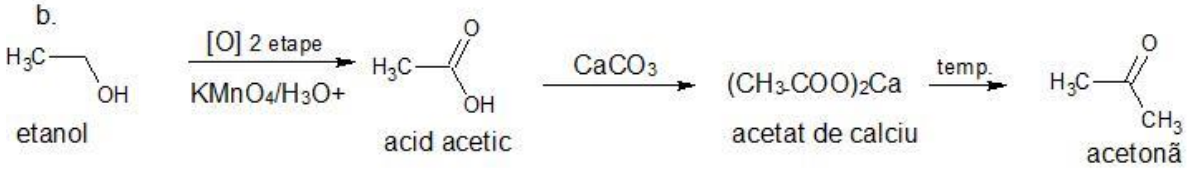
a. acid tricloracetic;
b. acetonă;
c. etan;
d. metan;
e. acid propanoic;
f. acid izobutiric;
g. acid malonic;
h. acid succinic.

Rezolvare:

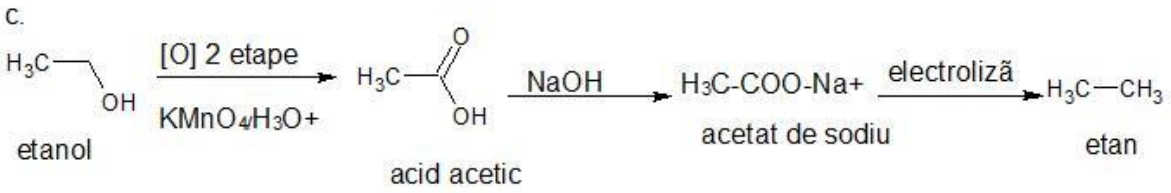
a.



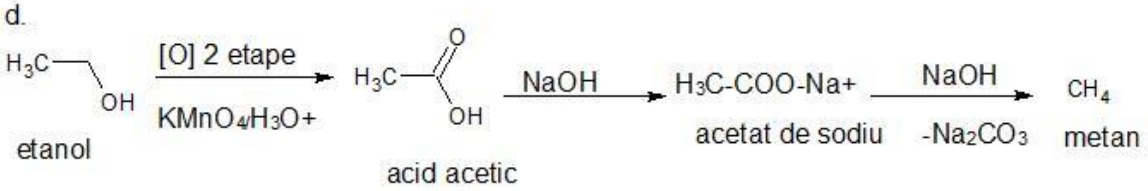
b.



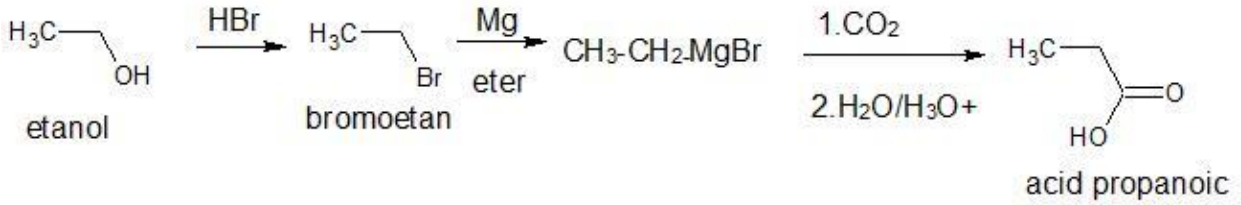
c.



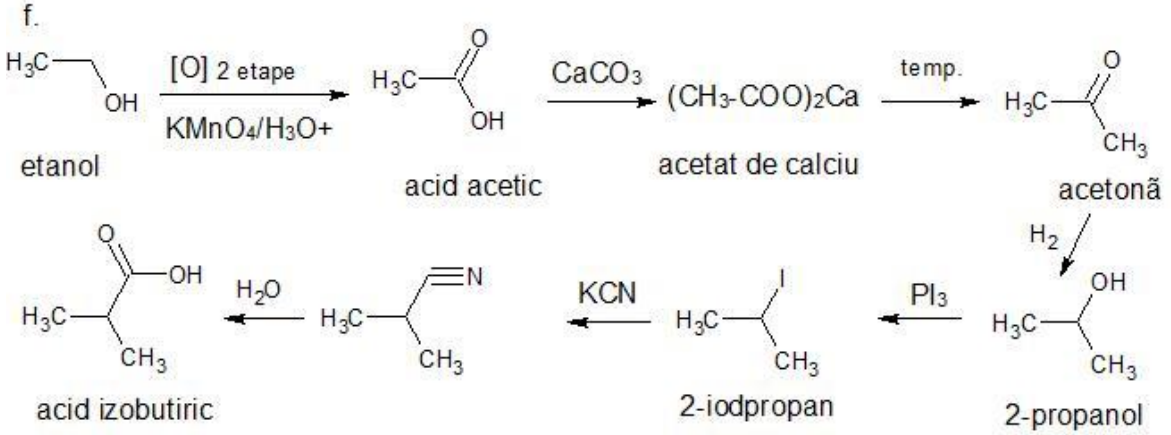
d.



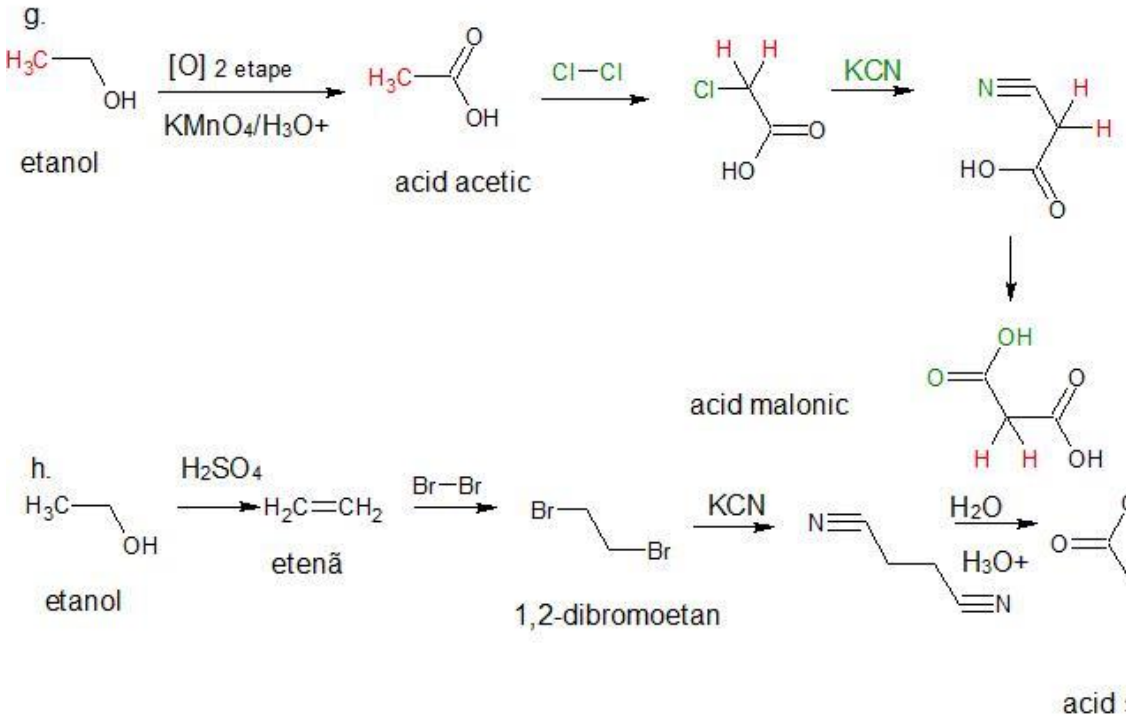
e.


HBr
Mg
eter
CH3-CH2-MgBr
1.CO2
2.H2O/H3O+
etanol
bromoetan
acid propanoic

f.


[O] 2 etape
KMnO4/H3O+
CaCO3
(CH3-COO)2Ca
temp.
etanol
acid acetic
acetat de calciu
acetonã
H2
PI3
KCN
H2O
2-propanol
2-iodpropan
acid izobutiric

g.


[O] 2 etape
KMnO4/H3O+
Cl—Cl
KCN
etanol
acid acetic
acid malonic

h.

H2SO4
Br—Br
KCN
H2O
H3O+
etanol
etenã
1,2-dibromoetan
acid succinic

5.6.4. Compusul **A** cu formula moleculară $C_7H_4N_2O_6$ dă prin decarboxilare un compus **B**.

Stabiliţi formula de structură a lui **A** care conduce prin decarboxilare la un singur compus **B**.

Rezolvare:

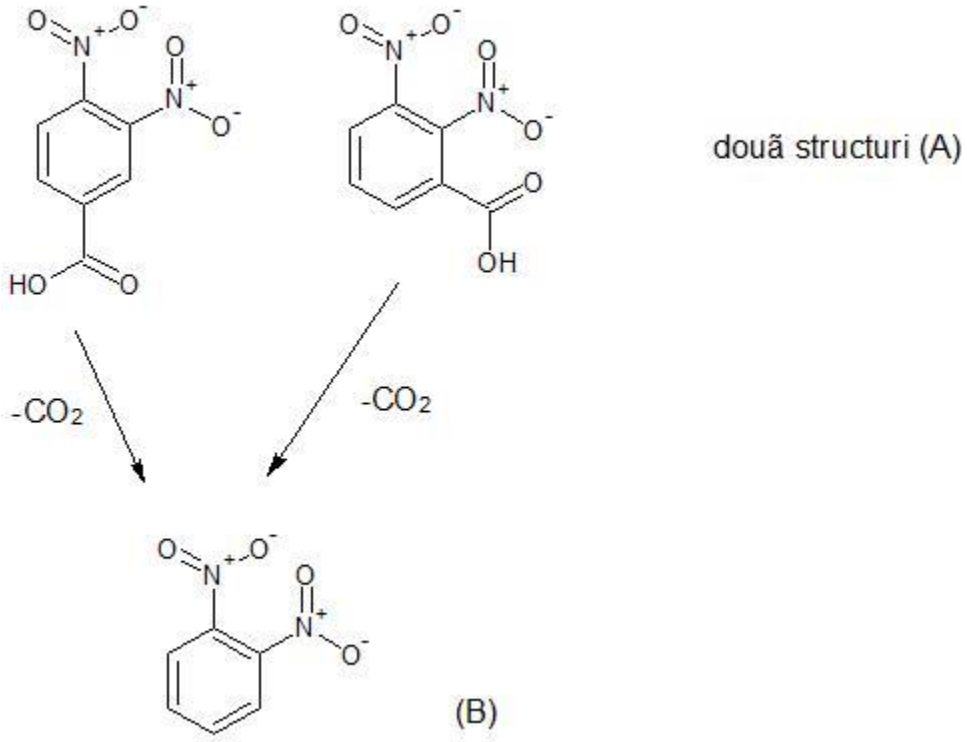
(A) $C_7H_4N_2O_6$ are N.E = 7

(B) $C_6H_4N_2O_4$ are N.E = 6

$C_7H_4N_2O_6$	⟶	$C_6H_4N_2O_4$	+	CO_2
(A)	decarboxilare	(B)		

Compus aromatic N.E. = 4 → $C_6H_4(NO_2)_2$ dinitrobenzen **(B)**

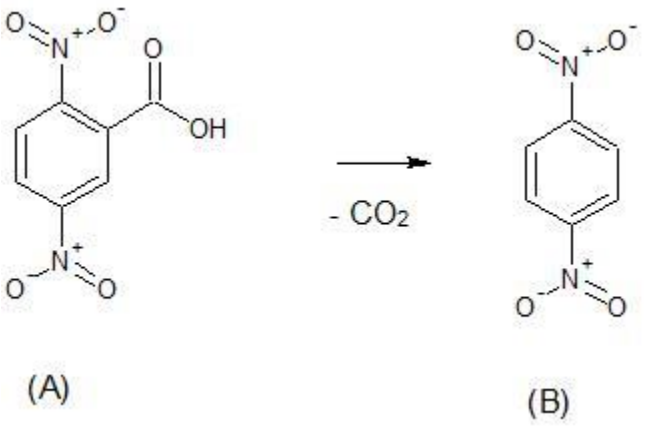
- Există **două structuri** posibile pentru **A** care prin decarboxilare conduce la **ortodinitrobenzen.**



două structuri (A)

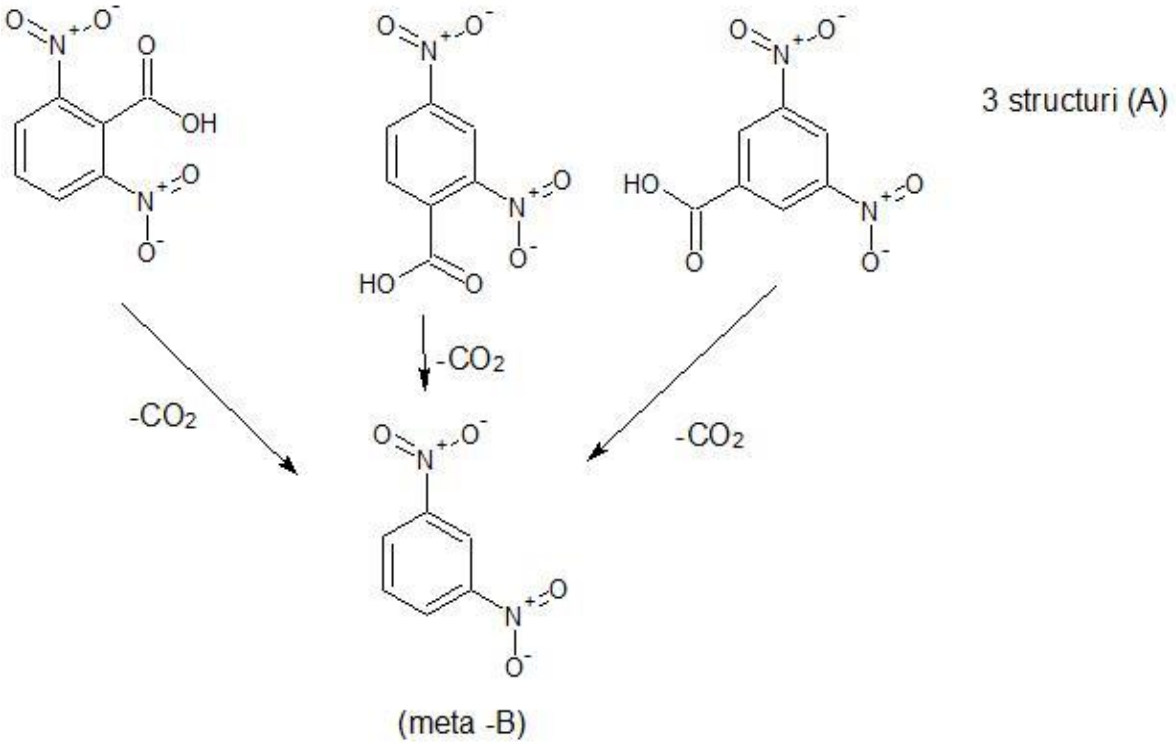
orto-B

- **Există o singură structură posibilă pentru A care prin decarboxilare conduce la paradinitrobenzen.**

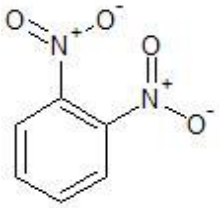
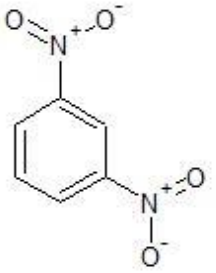
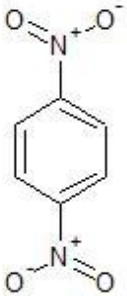


para-B (răspunsul corect)

- Există **trei structuri posibile** pentru **A** care prin decarboxilare conduce la **metadinitrobenzen**.



meta-B

(B)

orto, meta şi para – dintrobenzen (orto-B, meta-B şi para-B)

Răspunsul corect : acidul 2,5-dinitrobenzoic (A)

5.6. 5. 870 mg dintr-un acid **A** cu formula $C_6H_6O_6$ sunt neutralizaţi de 30 ml dintr-o soluţie 0,5 N de hidroxid de sodiu. Prin hidrogenarea lui **A** rezultă **B** ($C_6H_8O_6$). Ozonoliza lui **A** generează doi compuşi dintre care unul poate conduce la acid oxalic, iar altul **D** conduce prin reducere la acid succinic. Stabileşte formula structurală a lui **A.**

Rezolvare:

870 mg		m_d = 15*40 mg				
$C_6H_6O_6$	+	nNaOH	→			
acid **A**		hidroxid de sodiu				
174 mg		n*40 mg				

M $C_6H_6O_6$ = 6*12 + 6*1 + 6*16 = 174 mg/mmol

M NaOH = 23 + 16 + 1 = 40 mg/mmol

1000 ml soluţie NaOH ……0,5*40 g NaOH

30 ml soluţie NaOH…….. m_d g NaOH

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m_d = 30*0,5*40/1000 = 15*40/1000 g NaOH = 15*40 mg NaOH

$$\frac{870}{174} = \frac{15*40}{n*40}$$

$$\frac{870}{174} = \frac{15}{n}$$

5n = 15

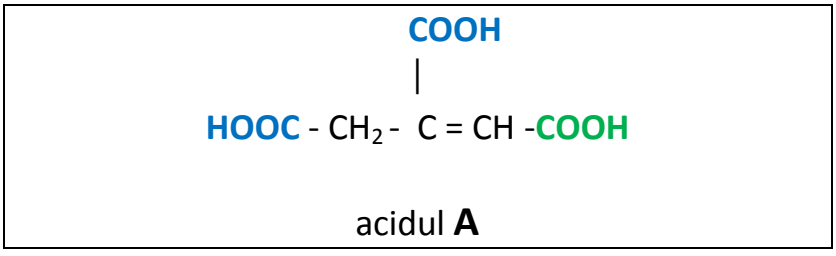
n = 3 deci **A** este un acid tricarboxilic : $C_3H_3(COOH)_3$

A + H_2 → **B**

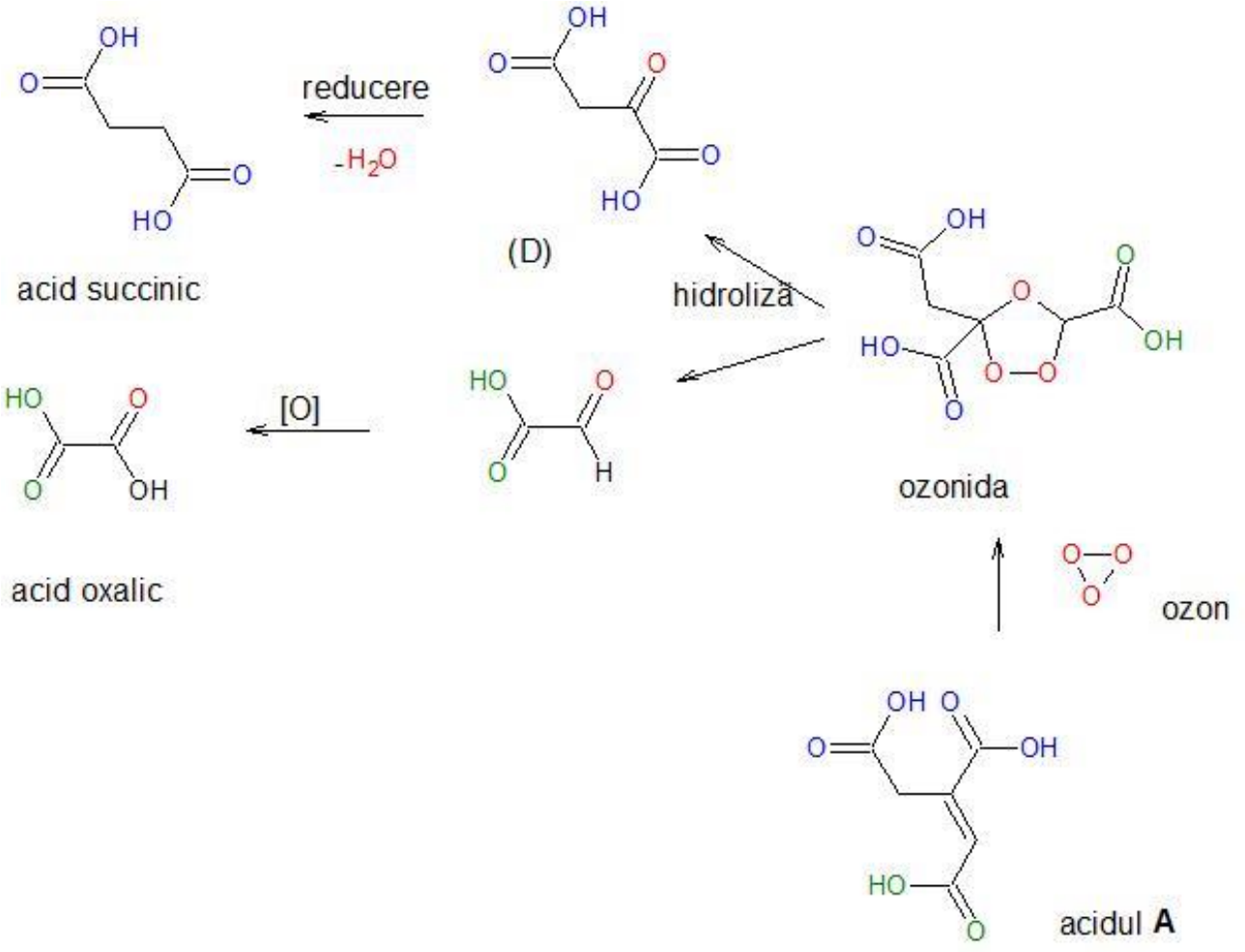
adică

$C_6H_6O_6$	+	H_2	→	$C_6H_8O_6$
A		hidrogen		B

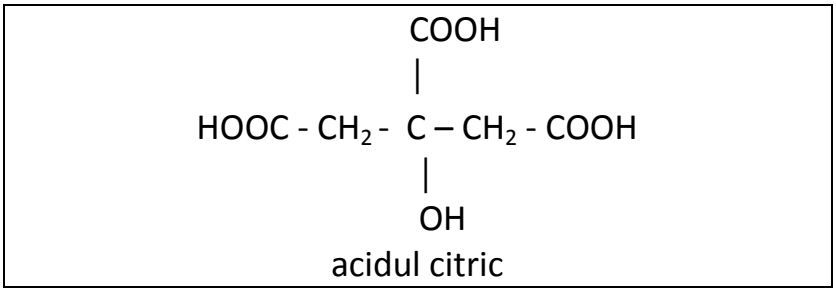
Deci A conţine o singură legătură dublă deoarece numărul de atomi de hidrogen creşte de la 6 la 8.



acidul **A**

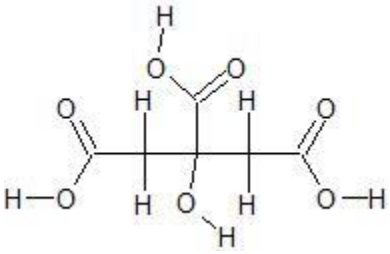


5.6. 6. Prin deshidratarea acidului citric

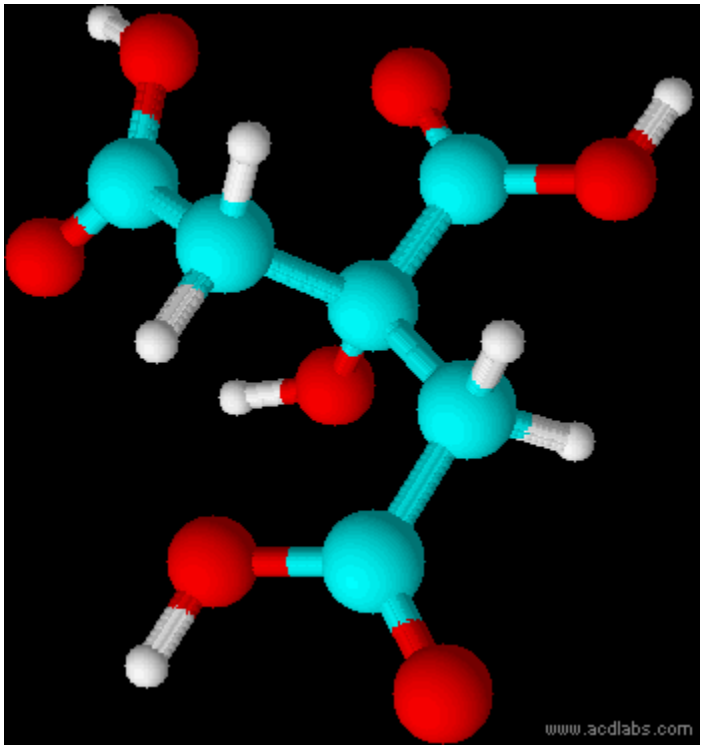


se obţine un acid **A**. Prin deshidratare şi decarboxilare acidul **A** conduce la două anhidride izomere. Aceste anhidride tratate cu apă generează acizii corespunzători **B** şi **D**. Oxidarea lui **B**

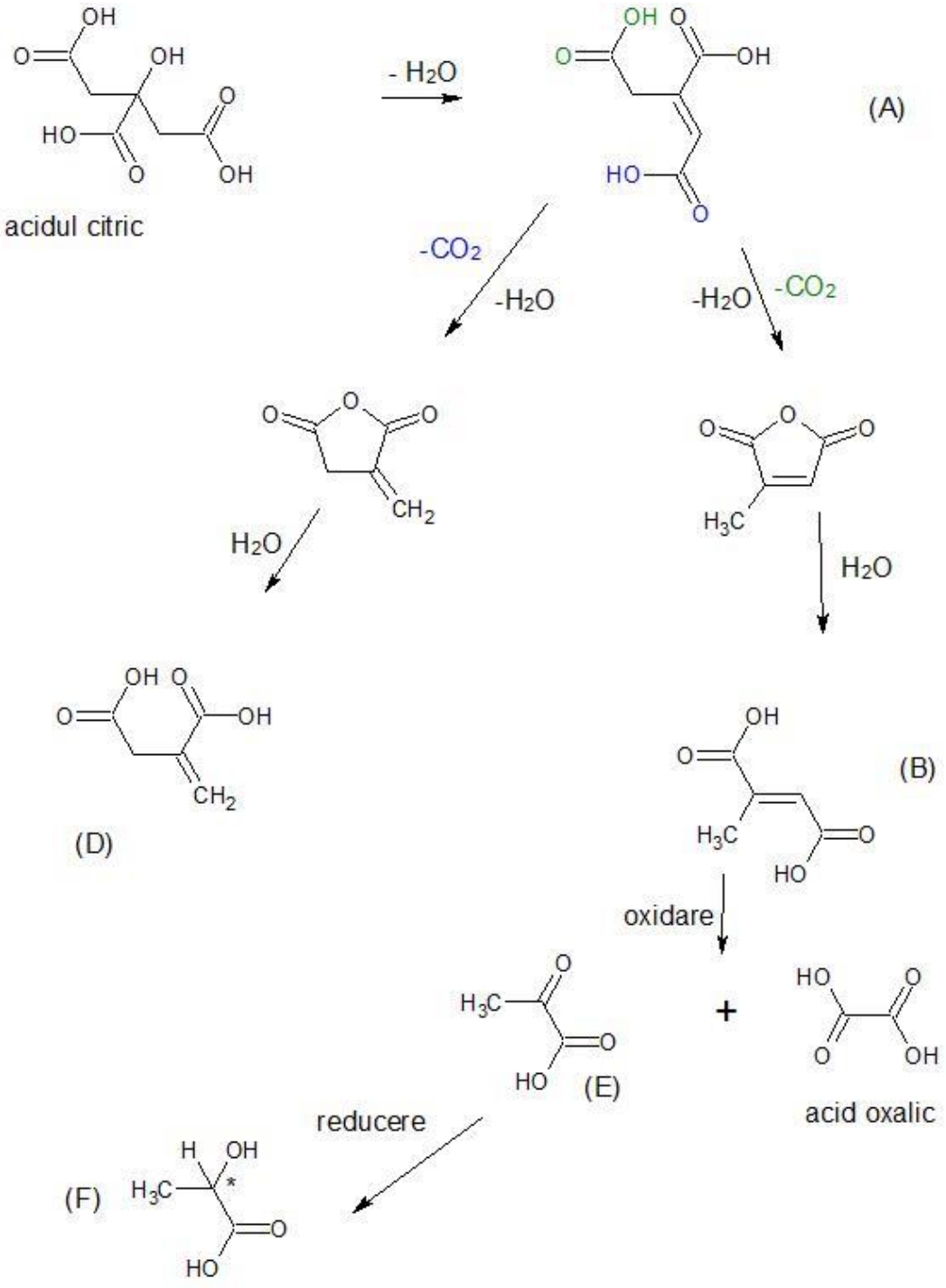
conduce la acid oxalic şi la compusul **E**. Reducerea lui **E** cu amalgam de sodiu şi apă conduce la produsul **F** care are un atom de carbon asimetric. Stabileşte formulele structurale ale compuşilor **A – F**.



acidul citric



acidul citric



* carbon asimetric