DEUG SV2-BG (C4)
Chimie organique (2 heures)

L'étudiant vérifiera si le sujet qui lui a été remis comporte 1 feuille recto-verso **"Enoncés"** et 1 feuille recto-verso **"Réponses".** Il devra donc reporter impérativement son N° de place et son N° d'identité sur la page **"Réponses"** qu'il rendra en fin d'épreuve au surveillant, en signant la feuille d'émargement.

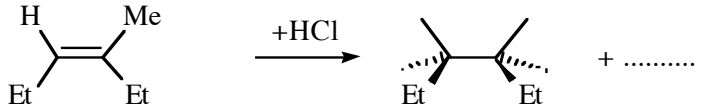
L'utilisation des calculettes est interdite.

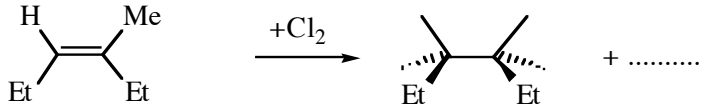
On utilisera les notations : -Me pour $-CH_3$, -Et pour $-C_2H_5$, -Ph pour $-C_6H_5$, -nBu pour $-C_4H_9$.

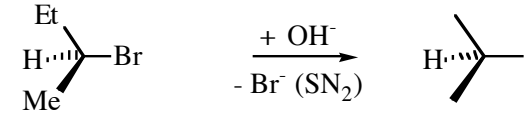
Enoncés

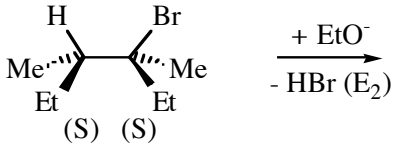
Problème I :

Quels sont les produits formés lors des quatre réactions données ci-dessous ? Donner la solution dans la case correspondante sur la feuille **"Réponses"** en précisant la stéréochimie des produits formés [géométrie (E/ Z), nature des carbones C* (R/S)]. Préciser par oui/non si les réactions sont stéréospécifiques et régiosélectives. Encadrer le ou les produits majoritaires obtenu(s) dans la réaction 1.

Réaction **1** 

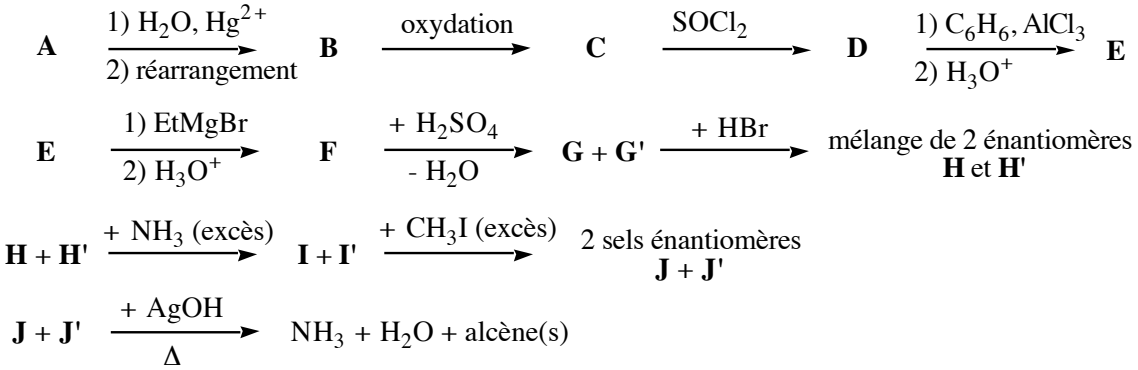
Réaction **2** 

Réaction **3** 

Réaction **4** 

Problème II :

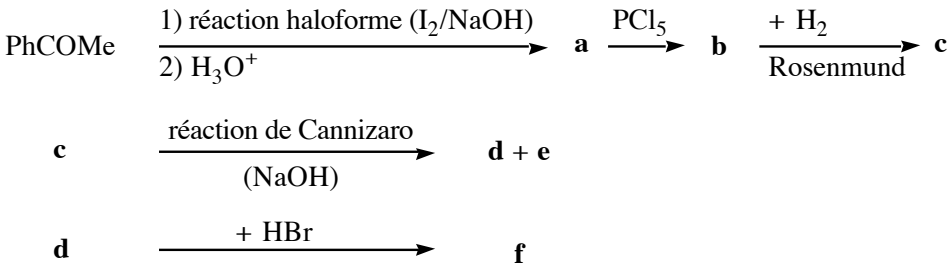
II-1) A partir de l'éthyne (ou acétylène) **A**, on réalise les transformations suivantes :



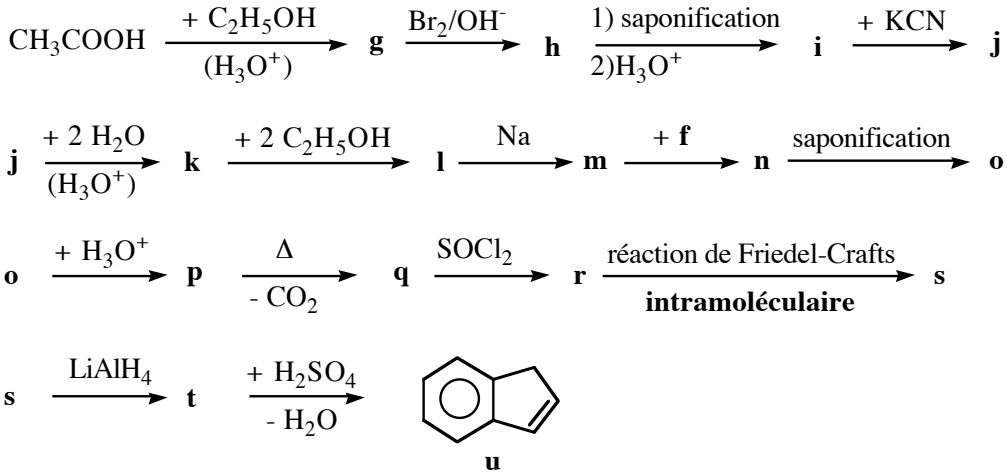
a) Identifier les composés (**A**) à (**J'**).

b) Donner la structure des alcènes obtenus à partir de (**J**) et (**J'**). Quel est l'isomère formé

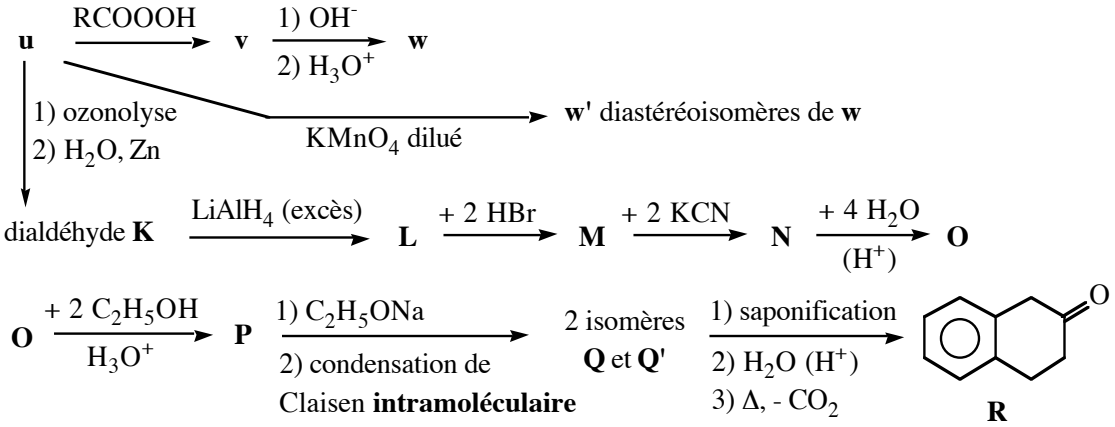
II-2) A partir de l'acétophénone (PhCOMe), on réalise les transformations suivantes :



Par ailleurs, au départ de l'acide éthanoïque, on prépare le malonate de diéthyle (**l**) selon :

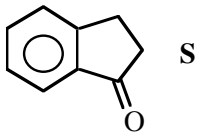


II-3) Au départ du composé (**u**), plusieurs réactions sont envisagées :

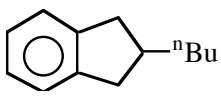


Question subsidiaire :
Donner un autre chemin réactionnel permettant d'accéder à (**R**) à partir de (**O**).

<u>Problème III :</u>
L'indanone (**S**) (ci-contre) en milieu EtO^-Na^+ fournit un carbanion (**T**) qui se condense sur la but-3-ène-2-one (**U**) conduisant, après une hydrolyse, à un mélange de 2 produits (**V**) et (**W**) dont (**V**) est nettement majoritaire. (**V**) est une dicétone racémique qui, soumise à une réduction selon Clemmensen, donne l'hydrocarbure aromatique (**X**) ci-contre.



S



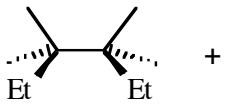
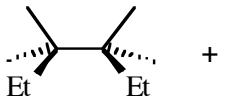
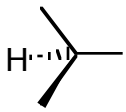
- Donner les structures de (**T**) à (**V**). Expliquer, au départ des formes de résonance respectives de (**U**), la prépondérance du composé (**V**) et du produit

Université de Bourgogne - DEUG SV2 - BG (C4) - Janvier 1999

N° Place | | | | N° Identité | | | | | | | | | Note | |

"**Réponses**" - (2 heures)

Problème I

Réaction	Nombre de stéréoisomères	Stéréospécifique (oui/non)	Régiosélectif (oui/non)
N°1	 +		
N°2	 +		
N°3			/
N°4			

Problème II-1

A	**B**	**C**	**D**	**E**
F	**G**	**G'**	**H**	**H'**
I	**I'**	**J**	**J'**	
Alcènes				

Problème II-2

a	**b**	**c**	**d**
e	**f**	**g**	**h**
i	**j**	**k**	**l**
m	**n**	**o**	**p**
q	**r**	**s**	**t**

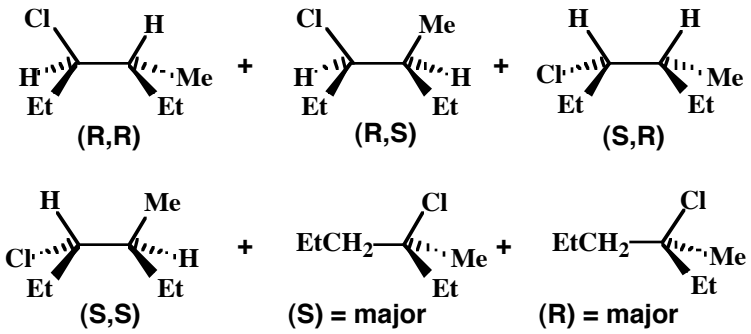
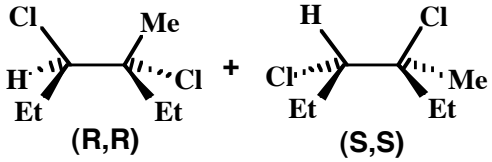
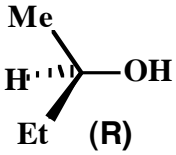
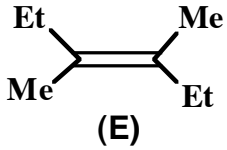
Problème II-3

v (2 énantiomères)	**w** (2 énantiomères)	**w'** (2 énantiomères)	**K**
L	**M**	**N**	**O**
P	**Q**	**Q'**	**R**
O $\xrightarrow{???}$ **R**			

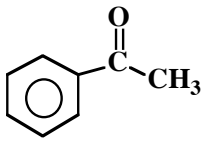
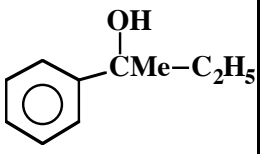
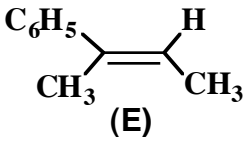
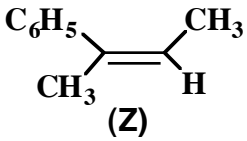
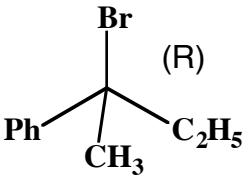
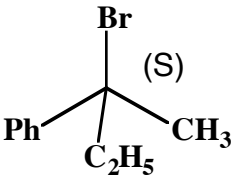
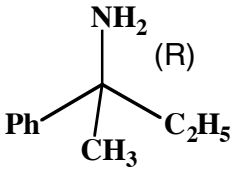
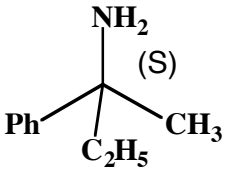
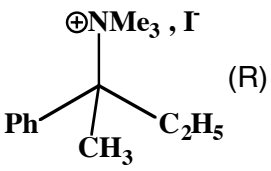
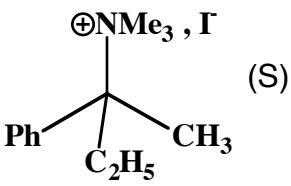
Problème III

T	**U**
Formules résonantes de **U**	
V	**W**

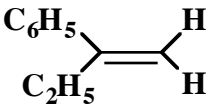
Problème I

Réaction	Nombre de stéréoisomères	Stéréospécifique (oui/non)	Régiosélectif (oui/non)
N°1	 (R,R) + (R,S) + (S,R) + (S,S) (S) = major (R) = major	NON	OUI
N°2	 (R,R) + (S,S)	OUI	NON
N°3	 (R)	OUI	/
N°4	 (E)	OUI	OUI

Problème II-1

A $HC\equiv CH$	**B** CH_3CHO	**C** CH_3COOH	**D** CH_3COCl	**E** 
F 	**G**  (E)	**G'**  (Z)	**H** 	**H'** 
I 	**I'** 	**J** 	**J'** 	

Alcènes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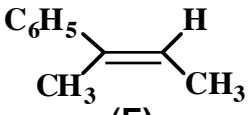
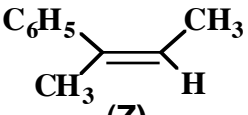

(E)


(Z)

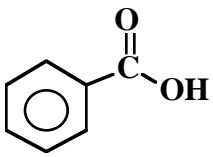
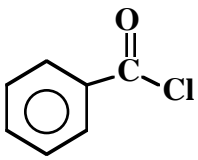
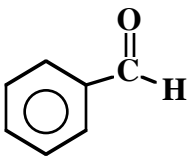
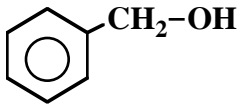
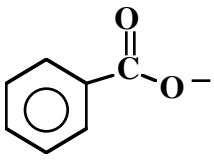
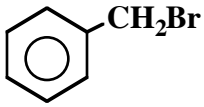
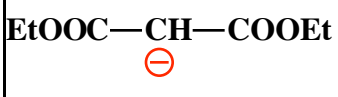
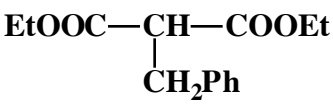
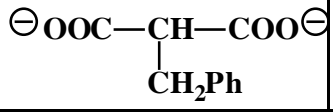
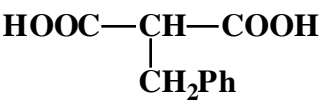
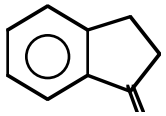
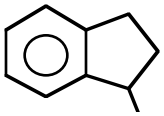
Règle de Hofmann
groupe partant volumineux (NMe_3)
donc on forme majoritairement
l'alcène le moins substitué

Mécanisme

1) $R\text{-}NR_3^+,I^- + AgOH \longrightarrow R\text{-}NR_3^+,OH^- + AgI$

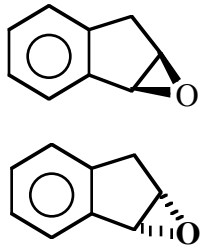
2) $R\text{-}NR_3^+,OH^- + OH^- \longrightarrow$ $+ NR_3 + H_2O$

Problème II-2

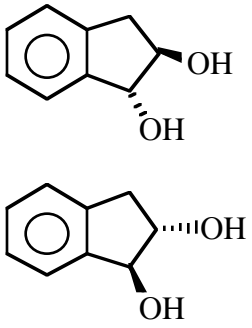
a 	**b** 	**c** 	**d** 
e 	**f** 	**g** CH_3COOEt	**h** $BrCH_2-COOEt$
i $BrCH_2-COOH$	**j** $NC-CH_2-COOH$	**k** $HOOC-CH_2-COOH$	**l** $EtOOCCH_2COOEt$
m 	**n** 	**o** 	**p** 
q $PhCH_2CH_2COOH$	**r** $PhCH_2CH_2COCl$	**s** 	**t** 

Problème II-3

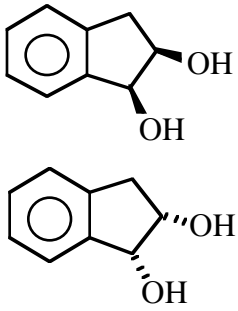
v (2 énantiomères)



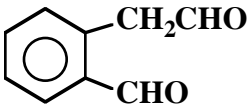
w (2 énantiomères)



w' (2 énantiomères)



K



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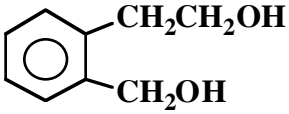

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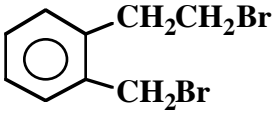

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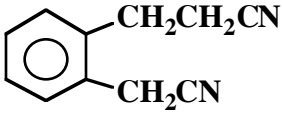

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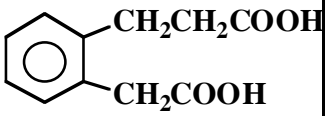

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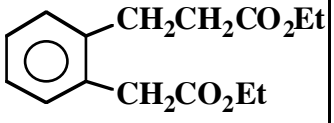

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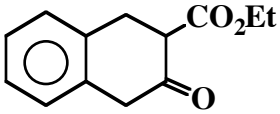

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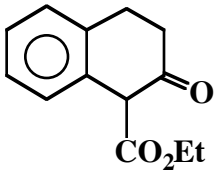

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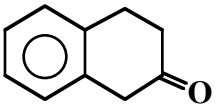

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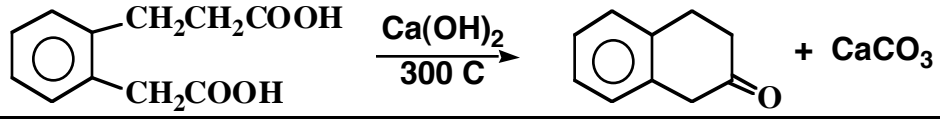
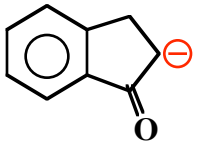


Problème III

T



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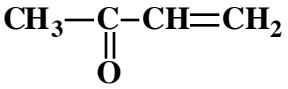

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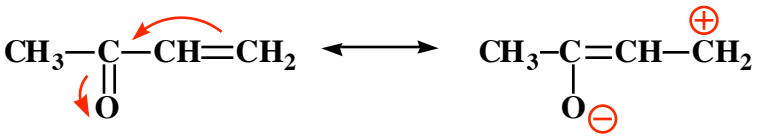

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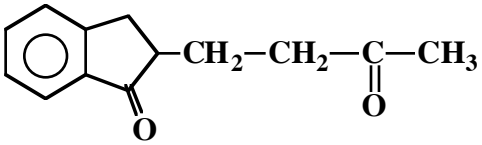
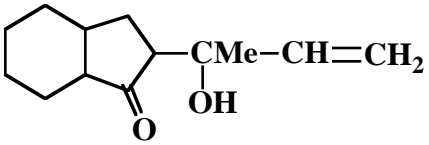
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