CHAPTER

23

Tautomerism

TAUTOMERISM

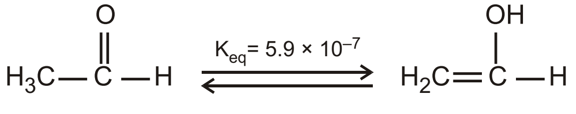
You may hear the word tautomers used to describe the relationship between enols and their corresponding carbonyl compounds. The term tautomers means "constitutional isomers that undergo such rapid interconversion that they cannot be independently isolated." Indeed under most common circumstances, carbonyl compounds and their corresponding enols are in rapid equilibrium. However, chemists now know that the interconversion of enols and their corresponding carbonyl compounds is catalyzed by acids and bases. This reaction can be very slow in dilute solution in the absence of acid or base catalysts, and indeed, enols have actually been isolated under very carefully controlled conditions.

Tautomerism is a special type of functional group isomerism which arises due to the transfer of H–atom as proton from a polyvalent atom to other polyvalent atom.

☞ The other names of tautomerism are **'desmotroprism'** or **'prototropy'.**

ENOLIZATION OF CARBONYL COMPOUNDS

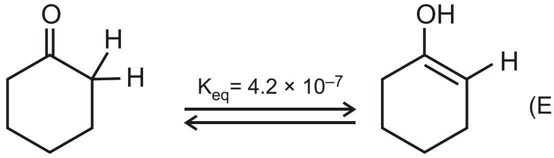
Carbonyl compounds with a-hydrogens are in equilibrium with small amounts of their enol isomers. The equilibrium constants shown in the following equations are typical.



$$H_3C-\overset{\overset{O}{\|}}{C}-H \xrightleftharpoons{K_{eq}= 5.9 \times 10^{-7}} H_2C{=}\overset{\overset{OH}{|}}{C}-H$$

acetaldehyde

acetaldehyde enol
(vinyl alcohol)



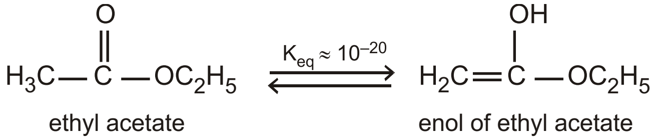
(Enol = 1.2% in liquid phase)

cyclohexanone

cyclohexanone enol

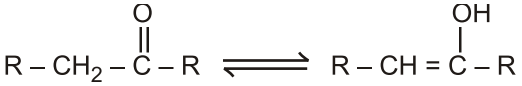
Unsymmetrical ketones are in equilibrium with more than one enol.

Ester contain even smaller amounts of enol isomers than aldehydes or keotnes.



$$H_3C-\overset{O}{\overset{\|}{C}}-OC_2H_5 \overset{K_{eq}\approx 10^{-20}}{\rightleftharpoons} H_2C=\overset{OH}{\overset{|}{C}}-OC_2H_5$$

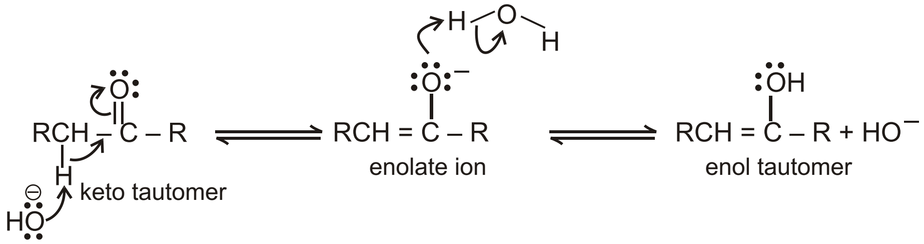
Mechanism of the tautomerism :



$$R-CH_2-\overset{O}{\overset{\|}{C}}-R \rightleftharpoons R-CH=\overset{OH}{\overset{|}{C}}-R$$

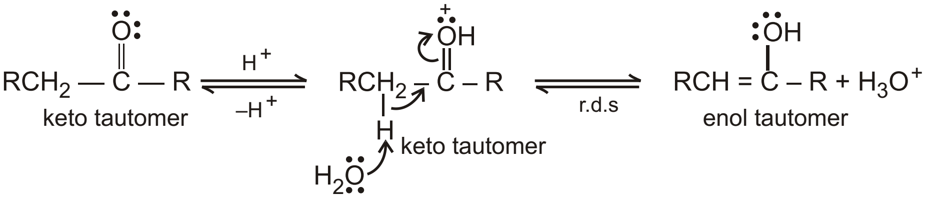
In a basic solution, hydroxide ion removes a proton from the -carbon of the keto tautomer, forming an enolate ion. Protonation on oxygen forms the enol tautomer, whereas protonation on the -carbon re-forms the keto tautomer.

BASE - CATALYZED KETO-ENOL INTERCONVERSION



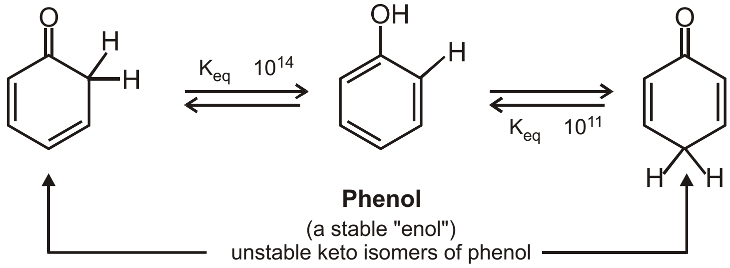
In an acidic solution, the carbonyl oxygen of the keto tautomer is protonated and water removes a proton from the -carbon, forming the enol.

ACID-CATALYZED KETO-ENOL INTERCONVERSION



The major reason for the instability of enols is that the C = O double bond of a carbonyl group is a stronger bond than the C = C double bond of a enol. With esters and acids, the additional instability of enols results from loss of the stabilizing resonance interaction between the carboxylate oxygen and the carbonyl electrons that is present in the carbonyl forms.

Some enols are more stable than their corresponding carbonyl compounds. Notice that phenol is conceptually an enol – a "vinylic alcohol." However, it is more stable than its keto isomers because phenol is aromatic.



DIFFERENCE BETWEEN TAUTOMERISM & RESONANCE

(a) In tautomerism, an atom changes place but resonance involves a change of position of pi-electrons or unshared electrons.

(b) Tautomers are different compounds and they can be separated by suitable methods but resonating structures cannot be separated as they are imaginary structures of the same compound.

(c) Two tautomers have different functional groups but there is same functional group in all canonical structures of a resonance hybrid.

(d) Two tautomers are in dynamic equilibrium but in resonance only one compound exists.

(e) Resonance in a molecule lowers the energy and thus stabilises a compound and decreases its reactivity but no such effects occur in tautomerism.

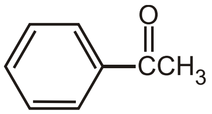
(f) In resonance, bond length of single bond decreases and that of double bond increases *e.g.*, all six C-C bonds in benzene are equal and length is in between the length of a single and a double bond.

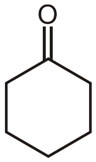
(g) Resonance occurs in planar molecule but atoms of tautomers may remain in different planes as well.

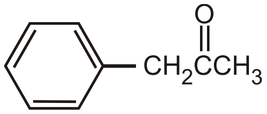
(h) Tautomers are indicated by double arrow $\rightleftharpoons$ in between the two isomers but double headed single arrow is put between the canonical (resonating) structures of a resonating molecule and effect of temperature and pressure is observed in tautomers.

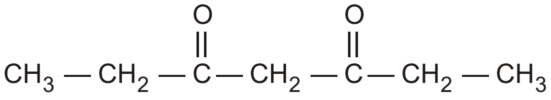
Solved Example

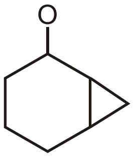
- Draw the most stable enol tautomers for each of the following compounds.

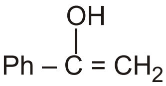
(a)


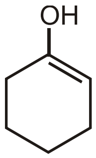
(b)


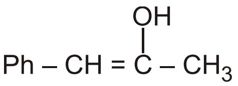
(c)


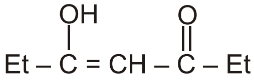
(d)

$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CH_3$

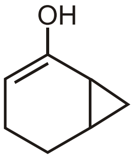
(e)


Sol. (a)

$Ph-\overset{OH}{\overset{|}{C}}=CH_2$

(b)


(c)

$Ph-CH=\overset{OH}{\overset{|}{C}}-CH_3$

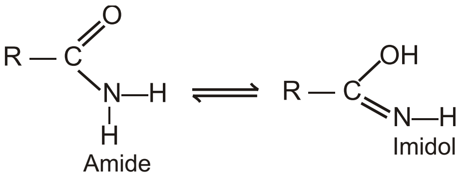
(d)

$Et-\overset{OH}{\overset{|}{C}}=CH-\overset{O}{\overset{\|}{C}}-Et$

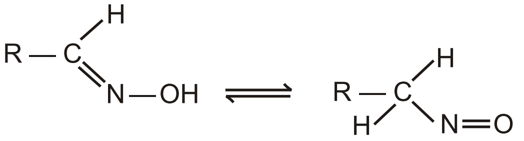
(e)


THREE ATOM TAUTOMERISM


$$\overset{H}{\diagdown}A-B=C \rightleftharpoons A=B-C\overset{H}{\diagup}$$

This type of Tautomerism is very prevalent, with one tautomer usually being much more stable than the other. For example, the summations of bond energies correctly predict the greater stabilities of amides, oximes, and aliphatic hydrazones overs the isomeric imidols, nitroso compounds, and aliphatic azo compounds, respectively.



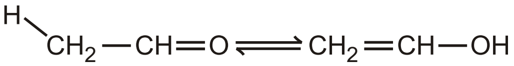


Oxime   Nitroso compound

$R_2C\quad N-NHR \rightleftharpoons R_2CH-N\quad N-R$

Hydrazone   Azo compound

Another common pair of tautomers is the ketone - enol couple.



$$H-CH_2-CH=O \rightleftharpoons CH_2=CH-OH$$

(i) Amidine system : $NH_2-CH\quad NH \rightleftharpoons HN\quad CH-NH_2$

(ii) Nitroso-oximino system : $CH_3-N\quad O \rightleftharpoons CH_2\quad N-OH$

(iii) Amido - imidol system : $NH_2-CH\quad O \rightleftharpoons HN\quad CH-OH$

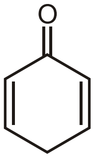
(iv) Azo-hydrazone system : $HN\quad N-CH_3 \rightleftharpoons HN-N\quad CH_2$

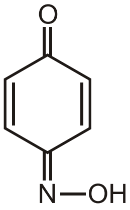
(v) Diazo-nitrosamine system : $Ar-N\quad N-OH \rightleftharpoons Ar-NH-N\quad O$

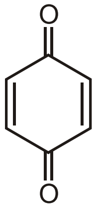
(vi) Diazo-amino (triazen) system : $HN\quad N-NH_2 \rightleftharpoons NH_2-N\quad NH$

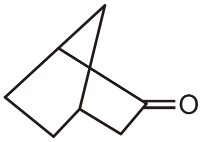
Solved Example

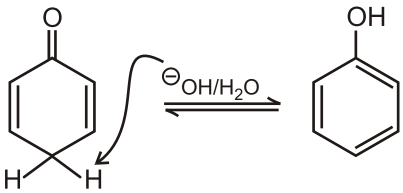
- Which of the following compounds are capable to undergo tautomerism in base catalysed medium?

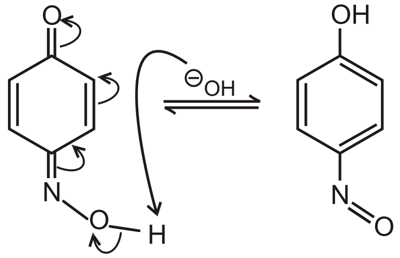
(1)


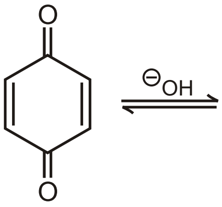
(2)


(3)


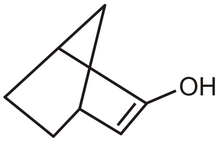
(4)


Sol. (1)


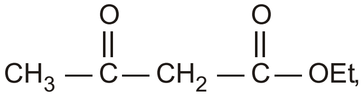
(2)


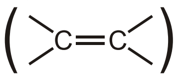
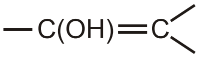
(3)


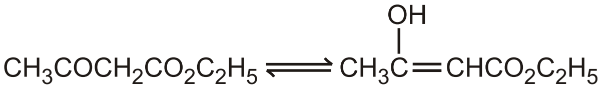
No tautomerism

(4)


EXPERIMENTAL EVIDENCE

Acetoacetic ester  $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OEt$, was first discovered by Geuther (1863), who prepared it by the action of sodium on ethyl acetate, and suggested the formula $CH_3C(OH) = CHCO_2C_2H_5$ (-hydroxycrotonic ester). In 1865, Frankland and Duppa, who, independently of Geuther, also prepared acetoacetic ester by the action of sodium on ethyl acetate, proposed the formula $CH_3COCH_2CO_2C_2H_5$ (-ketobutyric ester). These two formula immediately gave rise to two schools of thought, one upholding the Geuther formula, and the other the Frankland-Duppa formula, each school bringing forward evidence to prove its own claim.

1. **Experimenal evidence in favour of the Geuther fomula :**
   (i) When acetoacetic ester is treated with an ethanolic solution of bromine, the colour of the latter is immediately discharged. This indicates the presence of an olefinic double bond 
   (ii) When acetoacetic ester is treated with sodium, hydrogen is evolved and the sodium derivative is formed. This indicates the presence of a hydroxyl group (– OH group).
   (iii) When acetoacetic ester is treated with ferric chloride, a reddish-violet colour is produced.
   This is characteristic of compounds containing the group 
2. **Experimenal evidence in favour of the Frankland – Duppa formula test for (enol).**
   (i) Acetoacetic ester forms a cyanohydrin with hydrogen cyanide.
   (ii) Acetoacetic ester forms a bisulphite compound with sodium hydrogen sulphite.
   Controversy continued until about 1910, when chemists were coming to the conclusion that both formulae were correct, and that the two compounds existed together in equilibrium in solution.



$$CH_3COCH_2CO_2C_2H_5 \rightleftharpoons CH_3\overset{OH}{\overset{|}{C}}=CHCO_2C_2H_5$$

DIRECTION OF EQUILIBRIUM IN KETO–ENOL TAUTOMERISM

$$G^{\ominus} \quad H^{\ominus} \quad T\ S^{\ominus} \quad RT\ln K$$

keto $\rightleftharpoons$ enol ; K [enol] / [keto]

A knowledge of the values of the enthalpy and entropy changes would enable us to calculate $G^{\ominus}$ and from this, K, the equilibrium constant of the reaction :

The major reason for the instability of enols is that the C O double bond of a carbonyl group is a stronger bond than the C C double bond of a enol.

If the equilibrium mixture contains 1 per cent enol, then

$$G^{\ominus} = -5.7 \log 1/99 = 11.42 \text{ kJ}$$

If the equilibrium mixture contains 99 per cent enol, then

$$G^{\ominus} = -5.7 \log 99 = -11.42 \text{ kJ}$$

Thus difference of 22.84 kJ mol ^{1} in G shifts the equilibrium from 1 per cent enol to 99 per cent enol. It can therefore be seen that small changes in G will have large effects on the position of the equilibrium. Hence any attempt to calculate K from estimated values of H and S is almost certainly doomed to failure. However, a semi-quantitative approach is instructive. Any factors that affect $H^{\ominus}$ and $S^{\ominus}$ will affect the value of $G^{\ominus}$.

The sum of the bond energies of the $-CH_2CO-$ group is 1870 and that of the $-CH=C(OH)-$ group is 1820 kJ (from Table 2.2) :

2C – H(828.4) + C – C(347.3) + C = O (694.5) = 1870 kJ

C – H(414.2) + C = C(606.7) + C – O (334.7) + O – H (464.4) = 1820 kJ

This means that the enthalpy of formation of the CH_2CO group is –1870 kJ and that of the CH = C(OH) group is –1820 kJ. Thus the keto form is more stable than the enol by 50 kJ mol ^{1} and hence there must be some driving formce to bring about enolisation.

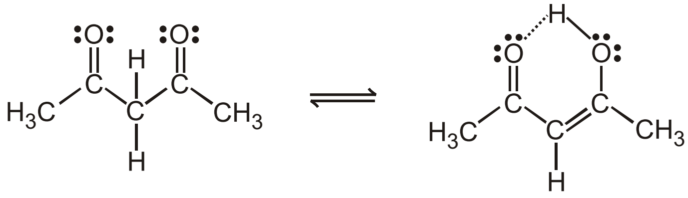
It's important that you understand that the keto form is way more stable than the enol form. (Typically, only 1 of every 100,000 to 10,000,000 molecules is in the enol form at any particular time.)

☑ SPECIAL TOPIC

GERO ENTROPY

Gero (1962) has found that cyclic monoketones contain more enol than the corresponding acyclic 2-one. In the cyclic ketones, change from keto to enol involves a relatively small change in strain in the ring due to the introduction of a double bond. For acyclic ketones, the introduction of the double bond has a much greater effect on the freedom to take up different conformations.

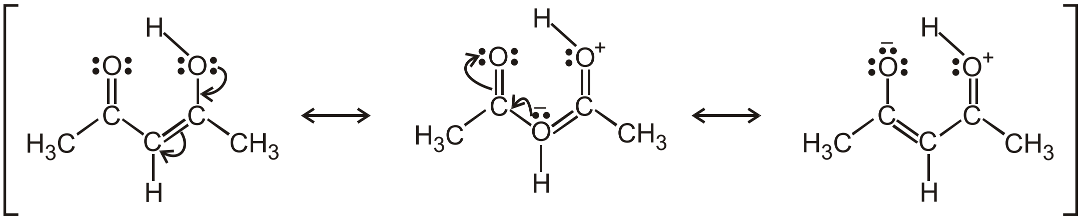
The enols of -dicarbonyl compounds are also relatively stable. (-Dicarbonyl compounds have two carbonyl groups separated by one carbon).



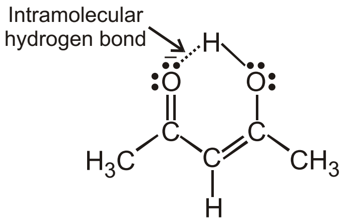
2,4-pentanedione
(acetylacetone)
(a b-dicarbonyl compound)

enol form
92% in hexane solution

There are two reasons for the stability of these enols. First, they are conjugated, but their parent carbonyl compounds are not. The resonance stabilization (-electron overlap) associated with conjugation provides additional bonding that stabilizes the enol.



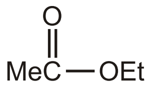
The second stabilizing effect is the intramolecular hydrogen bond present in each of these enols. This provides another source of increased bonding and hence, increased stabilization.



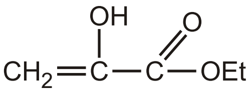
The enol form, in each case, is stabilised by intramolecular hydrogen bonding (say, 29.3 kJ mol ^{1}).

Now let us consider the resonance energies of crotonaldehyde (I), ethyl acetate (II) and ethyl

$MeCH{=}CHCHO$



$MeC(=O){-}OEt$



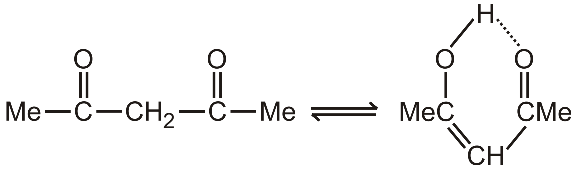
$CH_2{=}C(OH){-}C(=O){-}OEt$

R.E. (kJ0 (I) 10.40 (II) 75.35 (III) 75.35

methacrylate (III). The important point here is that in (III) the ethylenic bond does not enter into resonance with the CO_2Et group. (III) contains crossed conjugation, and the contribution to resonance is only the path that leads to the greater R.E., which , in this case, is the carbethoxy group.

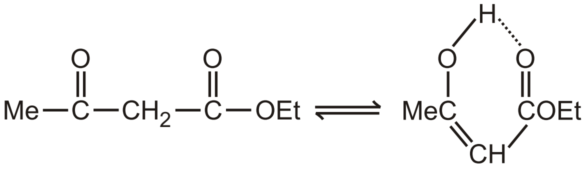
Consider the following equilibria :

Acetylacetone



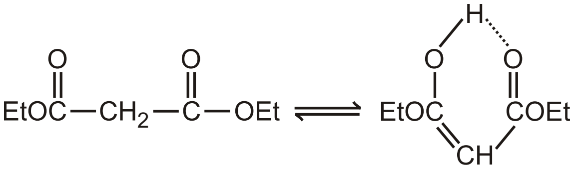
76 %

Ethyl acetoacetate



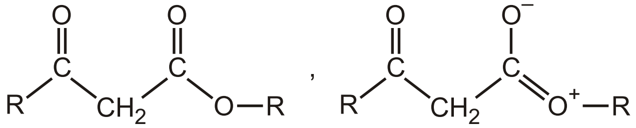
8 %

Ethyl malonate



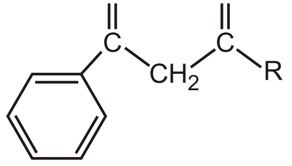
10 ^{3}%

When an OR group is substituted for one of the R groups in, thereby producing an acetoacetic ester, there is a decrease in enol content. This can be attributed largely to a cross conjugation between the ester group and the enol structure. The resonance of the ester group occurs at the expense of the resonance of the enol ring. This destabilizes the enol with respect to the keto tautomer and shifts the equilibrium toward the ketone. As to be expected, the diester ethyl malonate has even a smaller enol content (7.7 10 ^{3} per cent).

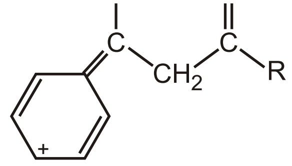


	Enol content	
$EtO—CO—CH_2—CO—OEt$	< 1%	
$CH_3—CO—CH_2—CO—OEt$	7.7	
$—CO—CH_2—CO—OEt$	21	
$CH_3—CO—CH_2—CO—CH_3$	76	
$—CO—CH_2—CO—CH_3$	89	= Ph
$—CO—CH_2—CO—$	100	

The substitution of a phenyl group increases the resonance energy of the keto as well as the enol tautomer, but much more so for the latter.



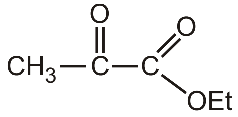
(a)



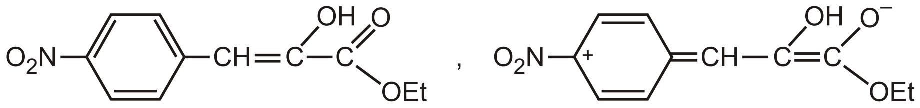
(b)

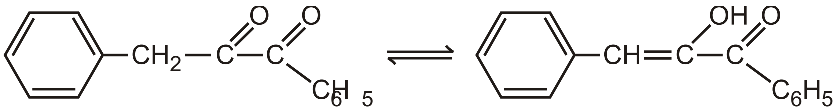
Consequently, diaroylmethanes, ($CO)_2CH_2$, are essentially 100 per cent enolic.

The effect of resonance in stabilizing the enols of -diketones is also demonstrable. For illustration, the enol content in ethyl pyruvate is too small to give a reaction with diazomethane. However, ethyl *p*-nitropyruvate is 42 per cent enolic in alcohol solution. Hence again the enol is stabilized by the “cinnamoyl” resonance energy. Other benzyl glyoxals have large enolic contents, too, and some range up to 100 per cent.

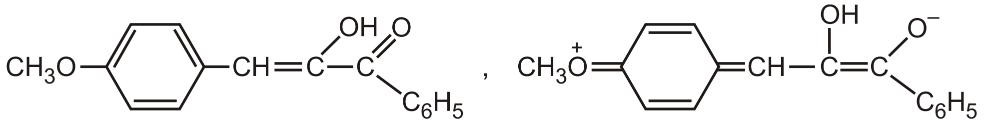


Ethyl pyruvate





30% enolic

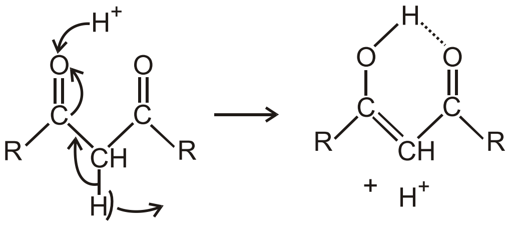


100% enolic

Table : Enol Content of some 1, 3-Diketones in various solvents

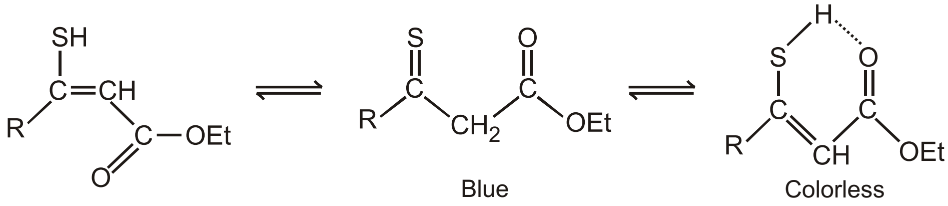
Diketone	Per cent enol	Solvent
$C_6H_5 — CS — CH_2 — CO_2 — C_2H_5$	95	Isooctane
	87	Ethanol
$CH_3 — CO — CH_2 — CO_2C_2H_5$	46.4	Hexane
	16.2	Benzene
	10.5	Ethanol
	10.1	Nitrobenzen
$CH_3 — CO — CH_2 — CO — CH_3$	92	Hexane
	15	Water
$CH_3 — CO — CH \quad — CO_2C_2H_5$	67	Hexane
	31	Water

Enolization probably takes place by ionization of an hydrogen atom and short electron - pair shifts. Therefore, the more electronegative are the groups attached to the a carbon atom, the easier it is for an hydrogen atom to escape as a proton. This expectation is fully substantiated in the substituted acetoacetic esters $CH_3CO — CHR — CO_2Et$, in which the enol content increases with increasing electronegativity of the R group.



R in $CH_3CO\underset{\substack{|\\ R}}{C}HCO_2Et$	Per cent enol (liquid)
C_2H_5	3
CH_3	4
H	7.5
C_6H_5	30
CO_2Et	44

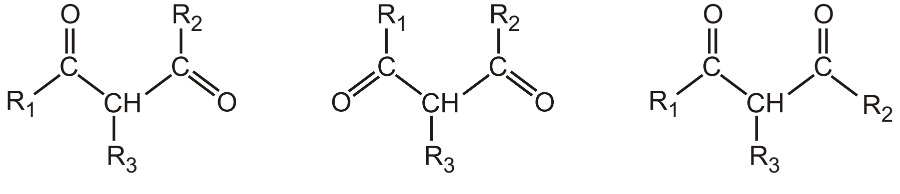
The inductive effect alone, however, is only a minor factor. For example, ethyl cyanoacetate has only a 0.25 per cent enol content. Another illustration is provided by the ketosulfones (RSO_2CH_2COR) and -disulfones ($RSO_2 — CH_2 — SO_2R$) which are hardly enolized at all and are weaker acids than the corresponding -diketones. The sulfones do not form chelates and the keto sulfones exhibit typical C = O infrared absorption and no O – H----O bands. On the other hand, thiobenzoylacetates are more enolic than the corresponding benzoylacetates.



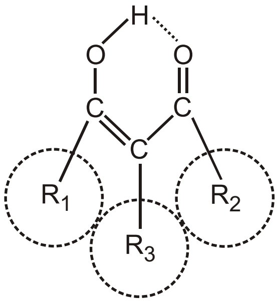
	Enol content (in alcohol)
$CH_3 — CO — CH_2 — CO_2Et$	11
$CH_3 — CS — CH_2 — CO_2Et$	41
$— CO — CH_2 — CO_2Et$	29(liq)
$— CS — CH_2 — CO_2Et$	87

The weakness of the C = S bond shifts the equilibrium in favor of the thioenol. Since the S – H --- O bond is not as strong as the O – H --- O bond, some of the thioenol exists in a nonchelated structure.

Steric and entropy effects : Finally, it can be shown that steric requirements and entropy changes can have a prolound effect upon the keto-enol equilibrium. A diketone $R_1 — CO — CHR_3 — CO — R_2$ may exist in several conformations.



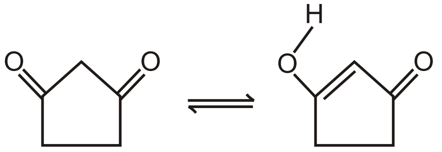
R in $R_1—CO—\underset{\substack{|\\ R_2}}{CH}—CO—R_3$	% Enol (liquid phase)
R_1 R_3 CH_3, R_2 H	76%
R_1 R_2 R_3 CH_3	44%
R_1 R_2 R_3 t B_4	0%



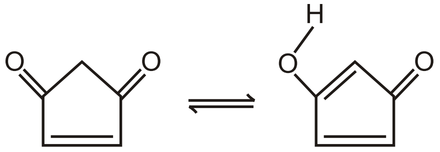
Compound	Per cent enol content	Compound	Per cent enol content
2-Butanone	0.12	3-Pentanone	0.07
2-Pentanone	0.01	3-Hexanone	0.05
2-Hexanone	0.11	3-Heptanone	0.17
2-Heptanone	0.10	3-Octanone	0.01
2-Octanone	0.92		

Ring size of cyclanone	Per cent enol content
4	0.55
5	0.09
6	1.18
7	0.56
8	9.3
9	4.0
10	6.1

It is interesting, in this connection, that cyclopentane-1,3-dione(LV) is completely enolic while cyclopenten-3, 5-dione (LVI) is completely ketonic. This further supports the notion that the cyclopentadienone is very unstable because of the bond - angle strain.



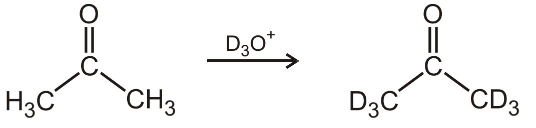
LV



LVI

REPLACEMENT OF HYDROGEN BY DEUTERIUM

Reaction of acetone with D_3O yields hexadeuterioacetone. That is, all the hydrogens in acetone are exchanged for deuterium. Review the mechanism of mercuric ion-catalyzed alkyne hydration and then propose a mechanism for this deuterium incorporation.



Acetone Hexadeuterioacetone

Acetone in deuterium oxide (D_2O) containing NaOD undergoes hydrogen-deuterium exchange and is transformed in successive steps into CD_3COCD_3 :

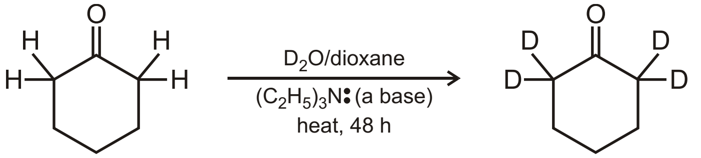
$$CH_3COCH_3 + DO^- \rightleftharpoons CH_3COCH_2\!:^- + HOD$$

$$CH_3COCH_2\!:^- + D_2O \rightleftharpoons CH_3COCH_2D + DO^-\!: \quad \text{etc.}$$

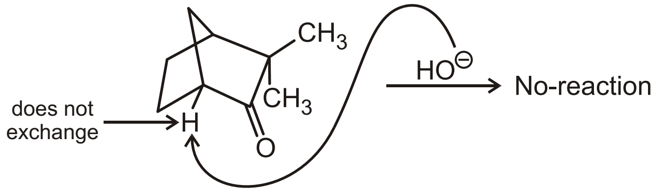
This exchange reaction is often of diagnostic value in determining the number of (replaceable) hydrogen atoms in an unknown carbonyl compound. Exchange of this kind, followed by analysis of the recovered compound for its deuterium content, shows the number of hydrogen atoms.

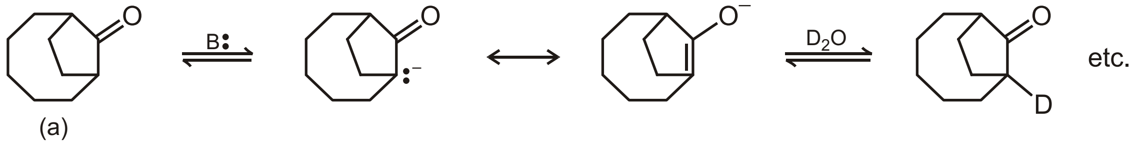
The acidities of aldehydes, ketones, and esters are particularly important because enolate ions are key reactive intermediates intermediates in many important reactions of carbonyl compounds. Let's consider the types of reactivity we can expect to observe with enolate ions.

First, enolate ions are Bronsted bases, and they react with Bronsted acids. The formation of enolate ions and their reactions with Bronsted acids have two simple but important consequences. First, the -hydrogens of an aldehyde or ketone – and no others – can be exchanged for deuterium by treating the carbonyl compound with a base in D_2O.

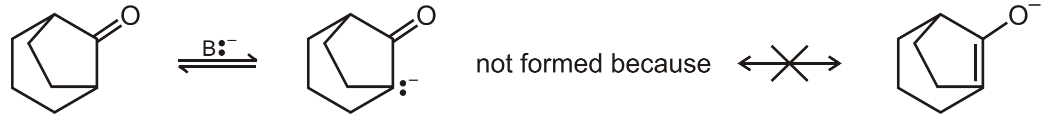


The following compound does not undergo base-catalyzed exchange in D_2O even though it has an -hydrogen because -hydrogen is less acidic - (Bredt's rule) is violated.





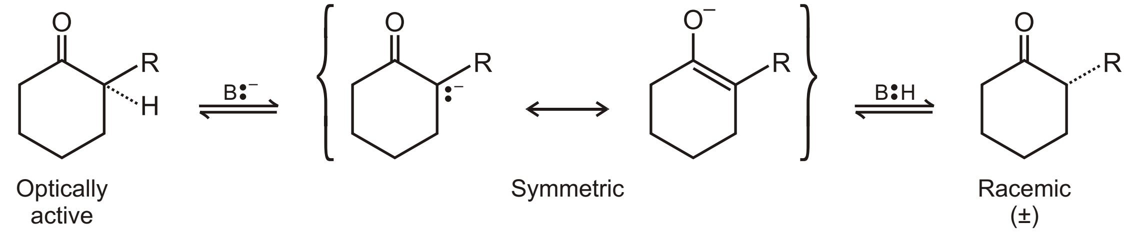
(a)



(b)

The non-exchangeability of the hydrogens in (b) is expressed in Bredt's rule, which states that a bicyclic compound cannot contain a double bond at a bridgehead. It is apparent that the rule does not apply when the ring system is large enough to accommodate the double bond, as in compound (a).

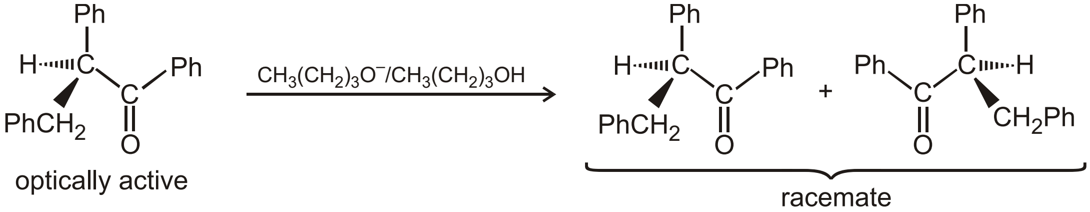
When the ketone (or aldehyde or ester) possesses an asymmetric carbon atom, the formation of the enolate anion destroys this asymmetry, with the result that optically active carbonyl compounds of this type are racemized by bases :



The symmetrical enolate anion can be reprotonated with equal probability to give either enantiomer.*

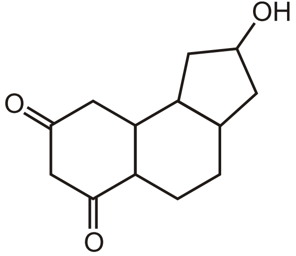
The equilibrium between the keto and enol forms is established by a deprotonation-protonation reaction that, when base catalyzed, can be regarded as proceeding via the enolate anion.

The second consequence of enolate - ion formation and protonation is that if an optically active aldehyde or ketone owes its chirality solely to an asymmetric -carbon, and if this carbon bears a hydrogen, the compound will be racemized by base.

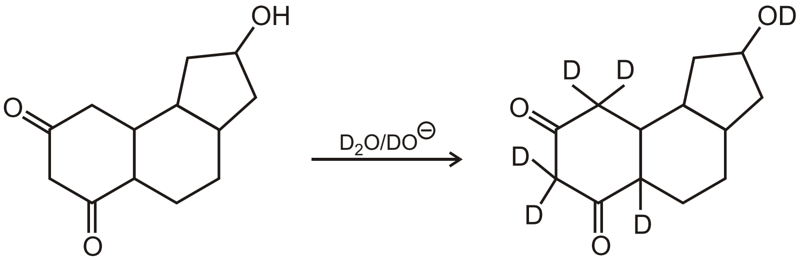


Solved Example

- Indicate which hydrogen(s) in each of the following molecules (if any) would be exchanged for deuterium following base treatement in D_2O :



Sol.



EXERCISE

SINGLE CHOICE QUESTIONS

1. Tautomers are :

(A) Structural isomers (B) Conformational isomers

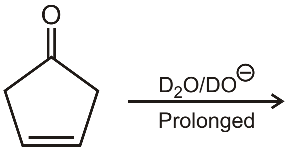
(C) Configurational isomers (D) Geometric isomers

2. Mixed ether are also known as :

(A) Symmetric ethers (B) Unsymmetric ethers

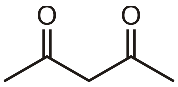
(C) Dialkyl ethers (D) Oxane

3. Number of hydrogen replaced by Deuterium in the given reaction are :



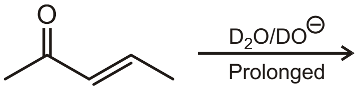
(A) 3 (B) 6 (C) 8 (D) 10

4. Total number of enol possible for the given compound are :



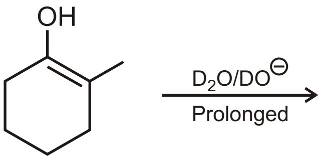
(A) 1 (B) 2 (C) 3 (D) 4

5. Number of hydrogen replaced by Deuterium in the given reaction are :



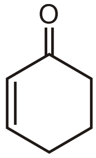
(A) 3 (B) 7 (C) 8 (D) 6

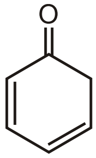
6. Number of hydrogen replaced by Deuterium in the given reaction are :

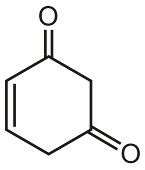


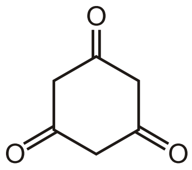
(A) 3 (B) 7 (C) 8 (D) 1

7. Which of the given compounds will have minimum enol content?

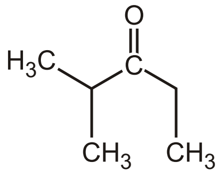
(A) 

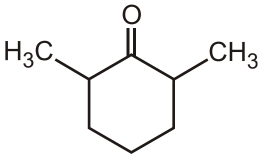
(B) 

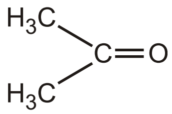
(C) 

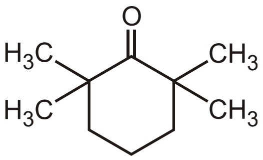
(D) 

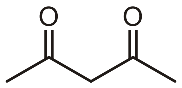
8. Which of the following compounds cannot exhibit keto-enol tautomerism?

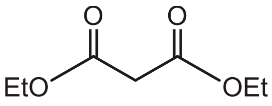
(A) 

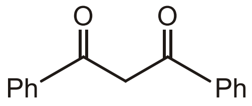
(B) 

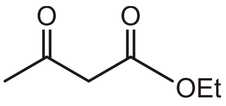
(C) 

(D) 

9. (I) 

(II) 

(III) 

(IV) 

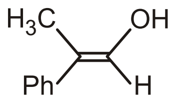
Correct order of enol content of given compound will be :

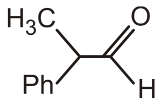
(A) III I IV II

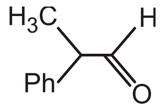
(B) IV II I III

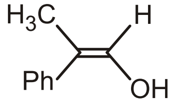
(C) II III I IV

(D) I III II IV

10. (I) 

(II) 

(III) 

(IV) 

Correct relationship between above compounds :

(A) II and III are Geometrical isomers

(B) I and II are Metamers

(C) III and IV are Tautomers

(D) I and IV are Tautomers

11. Tautomerism is also known as :

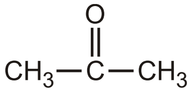
(A) Protropy

(B) Dynamic isomerism

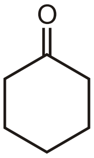
(C) Kryptomerism

(D) all of above

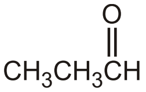
12. Maximum enol content is observed in :

(A) 

$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$

(B) 

(C) $CH_3COCH_2COCH_3$

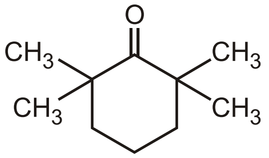
(D) 

$CH_3CH_3\overset{\overset{\displaystyle O}{\|}}{C}H$

13. Keto enol tautomerism is observed in :

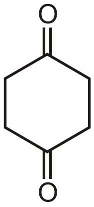
(A) C_6H_5CHO

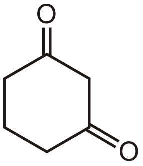
(B) $C_6H_5COC_6H_5$

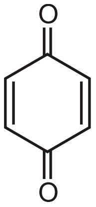
(C) 

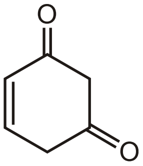
(D) $C_6H_5COCH_2 — COCH_3$

14. Keto enol tautomerism does not observed in :

(A) 

(B) 

(C) 

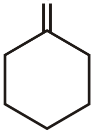
(D) 

15. Tautomer of which of the following can show geometrical isomerism :

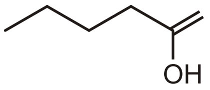
(A) $CH_3 — CHO$

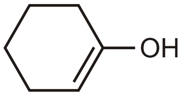
(B) $CH_3CH_2 — CHO$

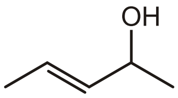
(C) $(CH_3)_2CH — CH$ O

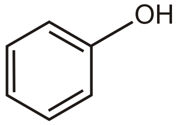
(D) 

16. Which of the following can't show Tautomerism?

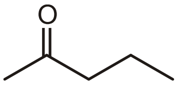
(A) 

(B) 

(C) 

(D) 

17. Number of enols of the given compound are :



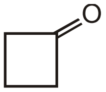
(A) 1

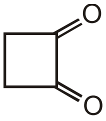
(B) 2

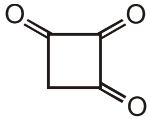
(C) 3

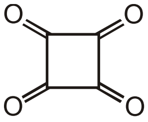
(D) 4

18. Maximum enol content is in which of the given compound :

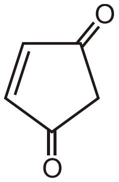
(A) 

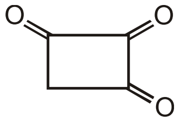
(B) 

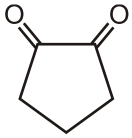
(C) 

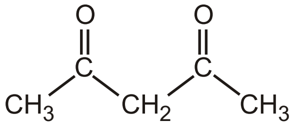
(D) 

19. Which of the following compounds has negligible enol?

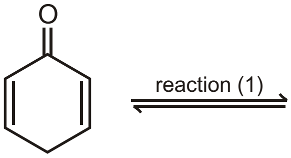
(A) 

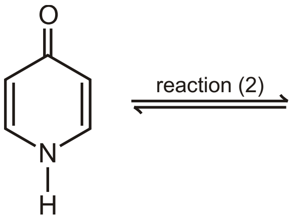
(B) 

(C) 

(D) 

20. Direction of equilibrium for the given reactions 1 and 2, respectively are :

(1) 

(2) 

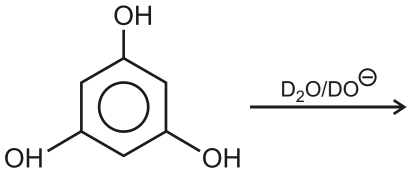
(A) forward, forward

(B) forward, backward

(C) backward, forward

(D) backward, backward

21. Number of hydrogen replaced by Deuterium in the given reaction are :

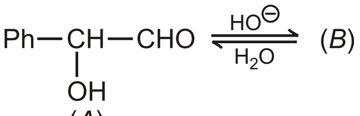


(A) 3

(B) 6

(C) 8

(D) 10

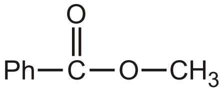
22. 

$$\mathrm{Ph-\underset{\underset{OH}{|}}{C}H-CHO}\ \underset{H_2O}{\overset{HO^{\ominus}}{\rightleftharpoons}}\ (B)$$

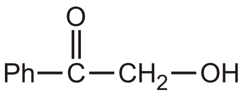
(*A*)

(*A*) & (*B*) are isomer and isomerization is effectively carried out by trace of base. Identify isomer (*B*).

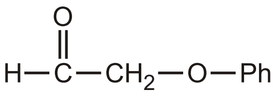
(A) $Ph-CH_2-CO_2H$

(B) 

$$\mathrm{Ph-\overset{\overset{O}{\|}}{C}-O-CH_3}$$

(C) 

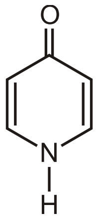
$$\mathrm{Ph-\overset{\overset{O}{\|}}{C}-CH_2-OH}$$

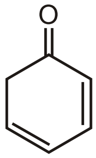
(D) 

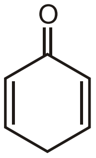
$$\mathrm{H-\overset{\overset{O}{\|}}{C}-CH_2-O-Ph}$$

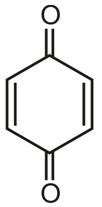
UNSOLVED EXAMPLE

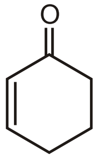
1. *X* Number of compounds which undergo Tautomerisation to form an Aromatic product.

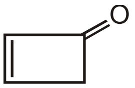
(a)


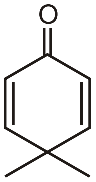
(b)


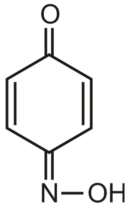
(c)


(d)


(e)


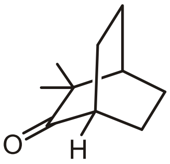
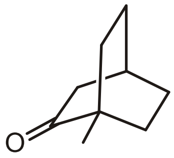
(f)


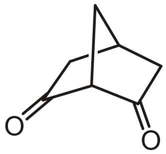
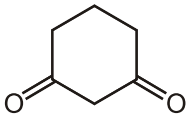
(g)


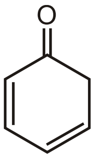
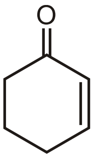
(h)


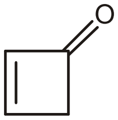
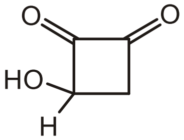
Find the value of *X*?

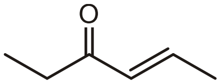
2. Which compound in each of the following pairs would be more extensively enolized?

(i)

and


(ii)

and


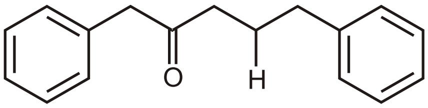
(iii)

and


(iv)

and


3. *Z* Number of deuterium exchanged on prolonged treatment of $\overset{\ominus}{O}D/D_2O$ with  . Find the value of *Z*?

SUBJECTIVE TYPE QUESTIONS

1. Treatment of this ketone with basic D_2O leads to rapid replacement of two hydrogen atoms by deuterium. Then, more slowly, all the other nonaromatic hydrogens except the one marked 'H' are replaced. How is this possible?

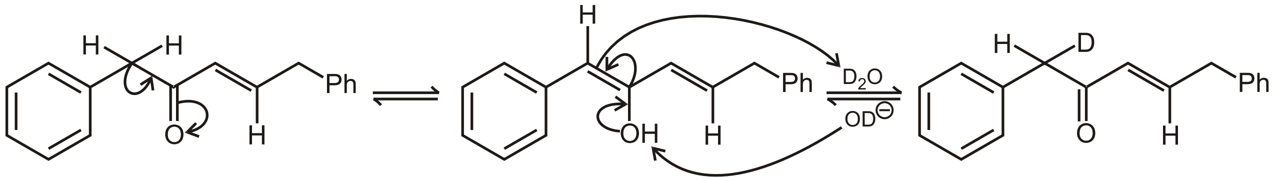


Purpose of the problem

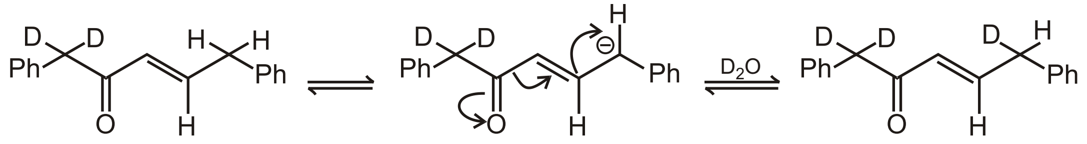
Working through the various ways in which enols and enolates can exchange hydrogen atoms.

Suggested solution

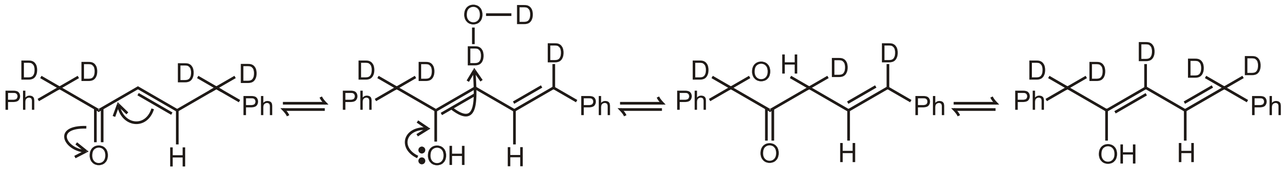
The protons on the group next to the ketone exchange by simple enolization and reversion to the ketone. Repetition of this process replaces both H atoms by D. Since D_2O is in large excess, the equilibrium favours D_2-ketone.



Next, enolization can occur at the other end of the molecule to form a dienol. This leads to replacement of the other CH_2 group with a CD_2 group after two exchanges.

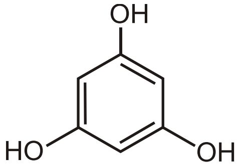


The same dienol can lead to exchange of the remaining proton by a more complicated series of reactions. Deuteration at the carbon atom next to the ketone and then loss of remaining proton back to the dienol is all that is needed.

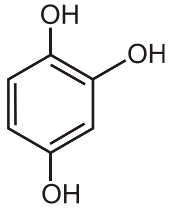


2. Which of the following two compounds will exhibit easy keto-enol tautomerism? Give explanation.

(a)

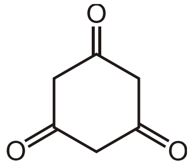


(b)

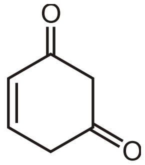


3. Which one of the following has higher enol content? Give reasons for your answer.

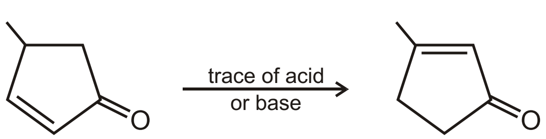
(a)

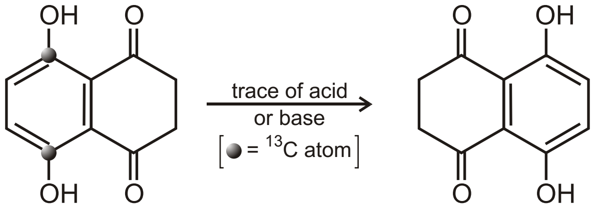


(b)



4. Draw mechanisms for these reactions using just enolization and its reverse.



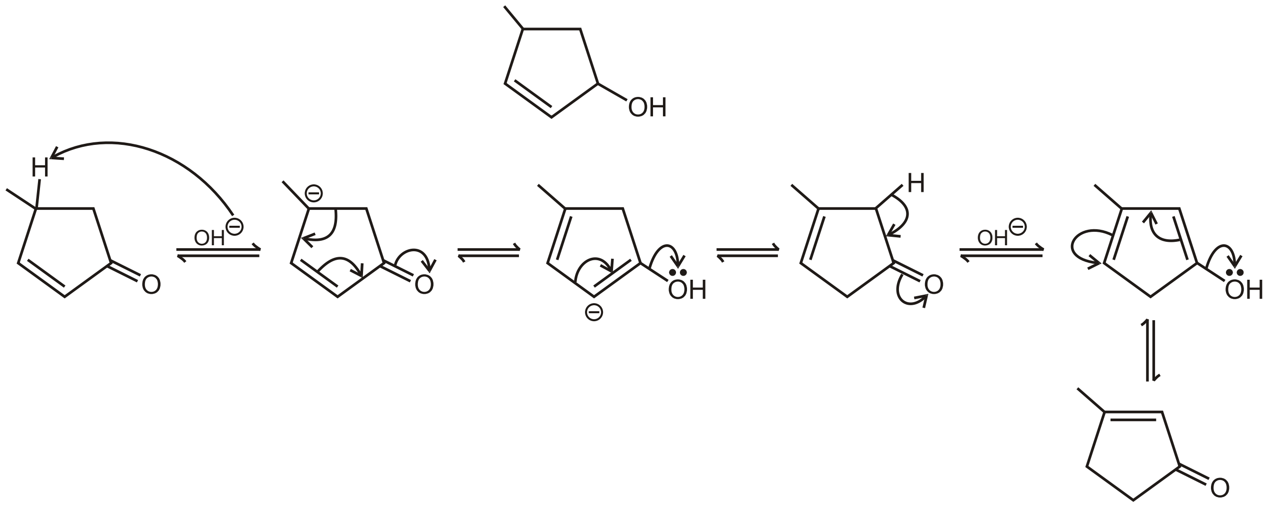


Purpose of the problem

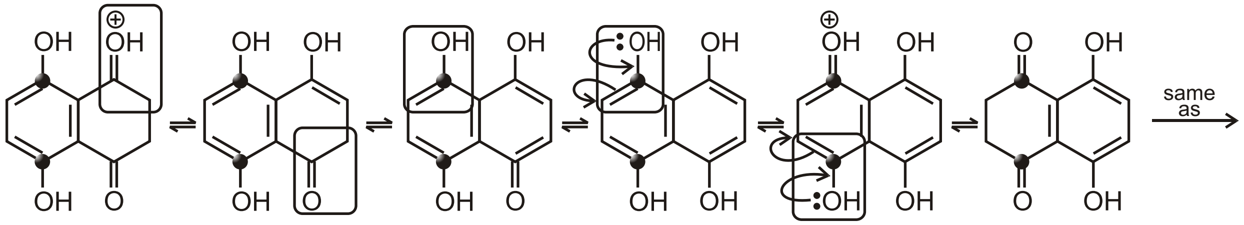
Exercise in using enolization of carry out simple reactions.

Suggested solution

Two enols are possible from the first compound: one (in the margin) leads back only to starting material but the other leads on to product. The whole system is in equilibrium favouring the enone with the more highly substituted alkene.



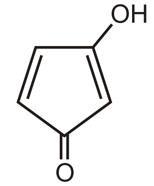
The second example is a bit of a trick. Of course, the ^{13}C label hasn't moved. The molecule just keeps enolizing and going back to a ketone until the functional groups is the two rings have changed places. Here we leave out the mechanism and just shown which ketones or enol are tautomerizing with a frame.



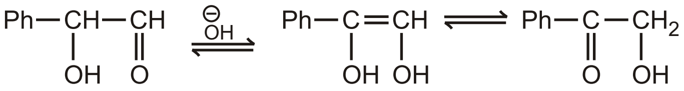
Answers

Single Choice Questions

1.	(A)	**2.**	(B)	**3.**	(B)	**4.**	(C)	**5.**	(B)	**6.**	(A)	**7.**	(A)	**8.**	(D)
9.	(A)	**10.**	(C)	**11.**	(A)	**12.**	(C)	**13.**	(D)	**14.**	(C)	**15.**	(B)	**16.**	(C)
17.	(C)	**18.**	(C)	**19.**	(A)	**20.**	(B)	**21.**	(B)	**22.**	(C)				

19. 

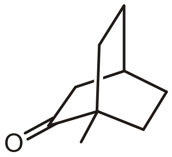
enol is anti-aromatic. No tautomerisation, 100% keto content.

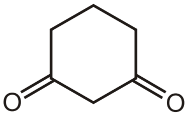
22. 

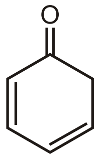
$$\mathrm{Ph-\underset{OH}{\underset{|}{CH}}-\underset{O}{\underset{\|}{CH}}} \xrightleftharpoons{\overset{\ominus}{OH}} \mathrm{Ph-\underset{OH}{\underset{|}{C}}=\underset{OH}{\underset{|}{CH}}} \rightleftharpoons \mathrm{Ph-\underset{O}{\underset{\|}{C}}-\underset{OH}{\underset{|}{CH_2}}}$$

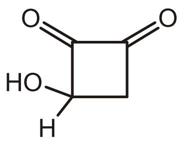
Unsolved Example

1. 4 (a,b,c,h)

2. (i) 

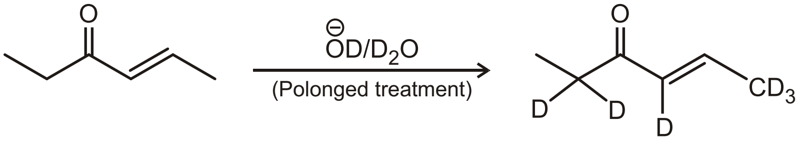
(ii) 

(iii) 

(iv) 

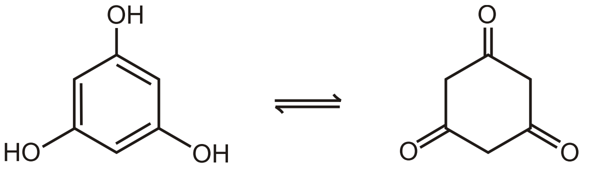
3. 6

Z 6

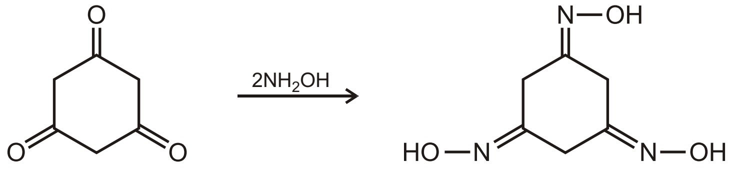


Subjective Type Questions

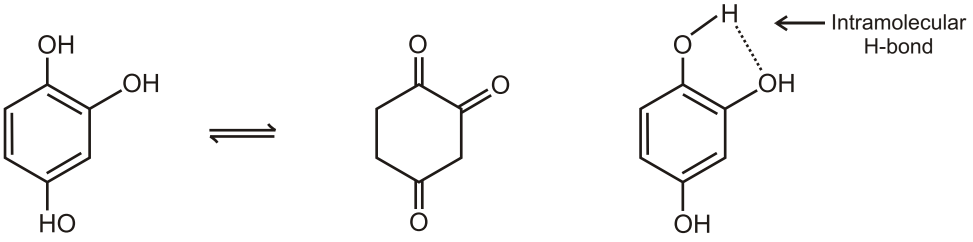
2. The compound 1, 3, 5-trihydroxybenzene (a) is trivially known as phloroglucinol. It exhibits easy keto-enol tautomerism. Its tri keto-form is known and reacts with hydroxylamine to give a trioxime. The loss of aromatic resonance energy of the benzene nucleus in phloroglucinol is counterbalanced by the bond energy of three C O groups, which is around 18 kcal/mol for each C O group.



Phloroglucinol 1, 3, 5-Cyclohexatrione



The compound (b) can also exhibit keto-enol tautomerism but the keto-form is very unstable due to the two C O groups on adjacent carbon atoms. The enol-form is stabilized by intramolecular hydrogen bonding. The structures are shown here.

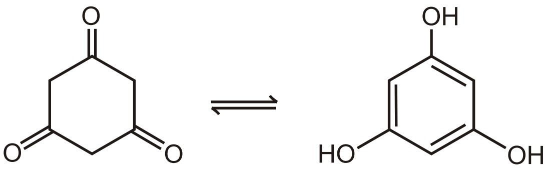


Hydroxyquinol
Enol-form (More stable)

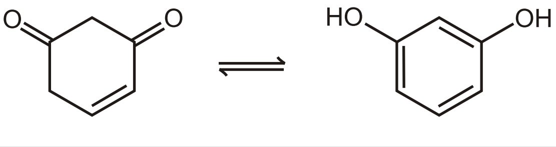
(Keto-form less stable)

3. The compound (a) is the triketo-form of phloroglucinol which is the enolic form. The enolic form of compound (b) is resorcinol. Now, phloroglucinol can readily form its triketo form. However, resorcinol cannot readily form its diketo form. Therefore, it can be concluded that enol-content of the compound is higher than that of (a).

(a)



(b)



❑❑❑