Paper-2

JEE Advanced, 2016

Part II: Chemistry

Read the instructions carefully:

General:

- 1. This sealed booklet is your Question Paper. Do not break the seal till you are instructed to do so.
- 2. The question paper CODE is printed on the left hand top corner of this sheet and the right hand top corner of the back cover of this booklet.
- 3. Use the Optical Response Sheet (ORS) provided separately for answering the questions.
- 4. The paper CODE is printed on its left part as well as the right part of the ORS. Ensure that both these codes are identical and same as that on the question paper booklet. If not, contact the invigilator.
- 5. Blank spaces are provided within this booklet for rough work.
- 6. Write your name and roll number in the space provided on the back cover of this booklet.
- 7. After breaking the seal of the booklet at 2:00 pm, verify that the booklet contains 36 pages and that all the 54 questions along with the options are legible. If not, contact the invigilator for replacement of the booklet.
- 8. You are allowed to take away the Question Paper at the end of the examination.

Optical Response Sheet

- 9. The ORS (top sheet) will be provided with an attached Candidate's Sheet (bottom sheet). The Candidate's Sheet is a carbon – less copy of the ORS.
- 10. Darken the appropriate bubbles on the ORS by applying sufficient pressure. This will leave an impression at the corresponding place on the Candidate's Sheet.
- 11. The ORS will be collected by the invigilator at the end of the examination.
- 12. You will be allowed to take away the Candidate's Sheet at the end of the examination.
- 13. Do not tamper with of mutilate the ORS. Do not use the ORS for rough work.

14. Write your name, roll number and code of the examination center, and sign with pen in the space provided for this purpose on the ORS. Do not write any of these details anywhere else on the ORS. Darken the appropriate bubble under each digit of your roll number.

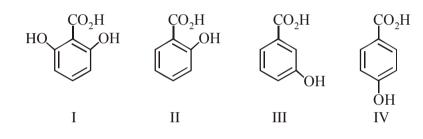
Darken the Bubbles on the ORS

- 15. Use a Black Ball Point Pen to darken the bubbles on the ORS.
- 16. Darken the bubble **O** completely.
- 17. The correct way of darkening a bubble is as:
- 18. The ORS is machine gradable. Ensure that the bubbles are darkened in the correct way.
- 19. Darken the bubbles only if you are sure of the answer. There is no way to erase or "undarken" a darkened bubble.

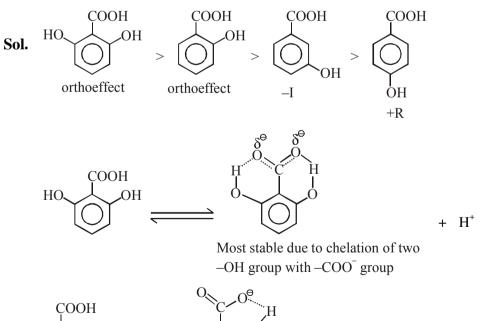
PART - II : CHEMISTRY

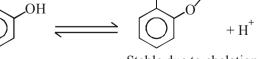
	SECTION-1 : (Maximum Marks : 18)					
•	This section contains SIX questions.					
•	Each question has FOUR options (A), (B), (C) and (D). ONLY ONE of these four options is correct.					
•	For each question,	, dark	ten the bubble corresponding to the correct option in the ORS.			
•	For each question, marks will be awarded in one of the following categories :					
	Full Marks :	+3	If only the bubble corresponding to the correct option is darkened.			
	Zero Marks :	0	If none of the bubbles is darkened.			
	Negative Marks :	-1	In all other cases.			

19. The correct order of acidity for the following compounds is :

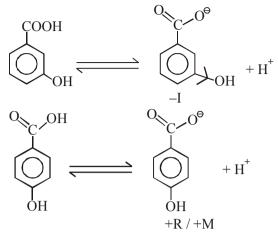


 $(A) I > II > III > IV \quad (B) III > I > II > IV \quad (C) III > IV > II > I \quad (D) I > III > IV > II$ Ans. (A)





Stable due to chelation of one -OH group with -COO⁻ group



- 20. The geometries of the ammonia complexes of Ni²⁺, Pt²⁺ and Zn²⁺, respectively, are :
 (A) octahedral, square planar and tetrahederal

 - (B) square planar, octahederal and tetrahederal
 - (C) tetrahederal, square planar and octahederal
 - (D) octahederal , tetrahederal and square planar

Sol.	Metal ion	Complex with NH ₃	Geometry
	Ni ²⁺	$[Ni(NH_3)_6]^{2+}$	Octahedral
	Pt ²⁺	$[Pt(NH_3)_4]^{2+}$	Square planar
	Zn ²⁺	$[Zn(NH_3)_4]^{2+}$	Tetrahedral

So, option (A) is correct.

21. For the following electrochemical cell at 298K,

Pt(s) | H₂(g, 1bar) | H⁺ (aq, 1M) || M⁴⁺(aq.), M²⁺(aq.) | Pt(s) E_{cell} = 0.092 V when $\frac{[M^{2+}(aq.)]}{[M^{4+}(aq.)]} = 10^x$

Given : $E^{0}_{M^{4+}/M^{2+}} = 0.151V$; 2.303 $\frac{RT}{F} = 0.059$

Thevalue of x is -

Ans. (D)

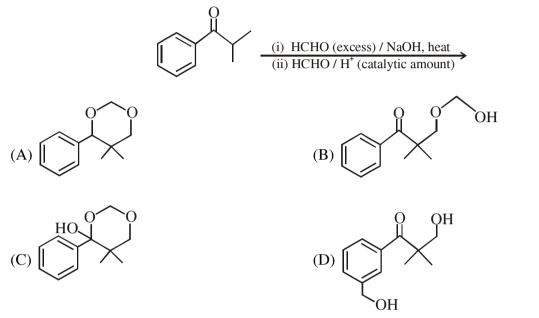
Sol. At anode :
$$H_2(g) = 2H^+ (aq) + 2e^-$$

At cathode : $M^{4+}(aq) + 2e^- = M^{2+} (aq)$
Net cell reaction : $H_2(g) + M^{4+} (aq) = 2H^+ (aq) + M^{2+} (aq)$
Now, $E_{cell} = \left(E_{M^{4+}/M^{2+}}^{\circ} - E_{H^+/H_2}^{\circ}\right) - \frac{0.059}{n} \cdot \log \frac{\left[H^+\right]^2 \left[M^{2+}\right]}{P_{H_2} \cdot \left[M^{4+}\right]}$

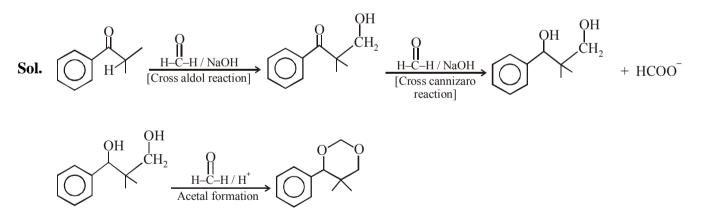
or,
$$0.092 = (0.151 - 0) - \frac{0.059}{2} \cdot \log \frac{1^2 \times [M^{2+}]}{1 \times [M^{4+}]}$$

$$\therefore \quad \boxed{[M^{2+}]}_{M^{4+}} = 10^2 \implies x = 2$$

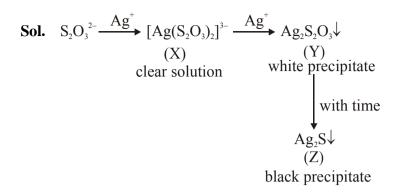
22. The major product of the following reaction sequence is :



Ans. (A)

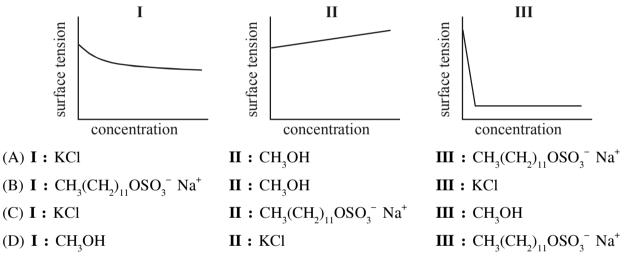


23. In the following reaction sequence in aqueous soluiton, the species X, Y and Z respectively, are -



So, X, Y and Z are $[Ag(S_2O_3)_2]^{3-}$, $Ag_2S_2O_3$ and Ag_2S respectively.

24. The qualitative sketches I, II and III given below show the variation of surface tension with molar concentration of three different aqueous solutions of KCl, CH_3OH and $CH_3(CH_2)_{11}OSO_3^-Na^+$ at room temperature. The correct assignment of the sketches is -



Ans. (D)

Sol. Water has large surface tension due to very strong interaction. Generally adding organic derivatives to water decreases its surface tension due to hydrophobic interaction.

In case III, hydrophobic interaction is stronger than case I causing surface tension to decrease more rapidly.

Due to K⁺Cl⁻ (inorganic electrolyte) intermolecular forces increases, surface tension increases.

	SECTION-2 : (Maximum Marks : 32)				
•	This section contains EIGHT questions.				
•	Each question has FOUR options (A), (B), (C) and (D). ONE OR MORE THAN ONE of these				
	four option(s) is (are) correct.				
•	For each question, darken the bubble(s) corresponding to all the correct option(s) in the ORS.				
•	For each question, marks will be awarded in one of the following categories :				
	<i>Full Marks</i> : +4 If only the bubble(s) corresponding to all the correct option(s) is (are) darkened.				
	<i>Partial Marks</i> : +1 For darkening a bubble corresponding to each correct option , Provided NO				
	incorrect option is darkened.				
	Zero Marks : 0 If none of the bubbles is darkened.				
	Negative Marks: -2 In all other cases.				

- for example, if (A), (C) and (D) are all the correct options for a question, darkening all these three will result in +4 marks; darkening only (A) and (D) will result in +2 marks; and darkening (A) and (B) will result in -2 marks, as a wrong option is also darkened.
- **25.** For 'invert sugar', the correct statement(s) is (are)

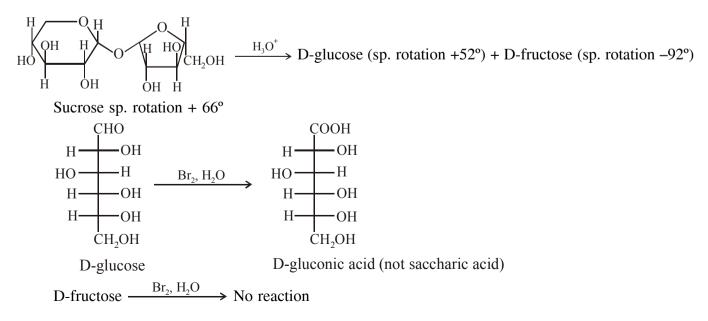
(Given : specific rotations of (+)-sucrose, (+)-maltose, L-(–)-glucose and L-(+)-fructose in aqueous solution are + 66° , +140°, -52° and + 92°, respectively)

- (A) 'invert sugar' is prepared by acid catalyzed hydrolysis of maltose
- (B) 'invert sugar' is an equimolar mixture of D-(+) glucose and D-(-)-fructose
- (C) specific rotation of 'invert surgar' is -20°
- (D) on reaction with Br_2 water, 'invert sugar' forms saccharic acid as one of the products

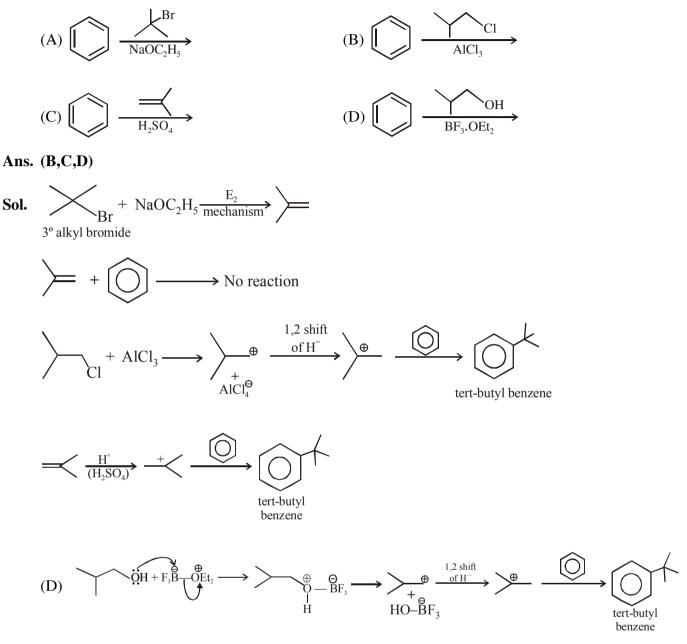
Ans. (B,C)

Sol. Invert sugar is equailmolar mixture of D-glucose and D-fructose which is obtained by hydrolysis of sucrose

Specific rotation of mixture is half of sum of sp. rotation of both components $\frac{+52^{\circ}+(-92^{\circ})}{2} = -20^{\circ}$



26. Among the following reaction(s) which gives (give) tert-butyl benzene as the major product is(are)



27. Extraction of copper from copper pyrite (CuFeS₂) involves

(A) crushing followed by concentration of the ore by froth-flotation

- (B) removal of iron as slag
- (C) self-reduction step to produce 'blister copper' following evolution of SO_2
- (D) refining of 'blister copper' by carbon reduction

Ans. (A,B,C)

Sol. Copper pyrite [CuFeS₂] Crushing into fine powder Concentrated by froth floatation process Roasting take place in reverberatory furnace $\begin{cases}
2CuFeS_2 + O_2 & \Delta \\
(air) \\
FeS + O_2 & \Delta \\
Smelting \\
FeO + SO_2
\end{cases}$ Smelting $\begin{bmatrix}
Iron is removed as slag of FeSiO_3 \\
FeO + SiO_2(flux) & \Delta \\
FeSiO_3(\ell)(slag)
\end{bmatrix}$ Copper matte (Cu₂S + FeS) $\begin{cases}
Self reduction \\
Self reduction \\
Cu_2S + 3O_2 & 2Cu_2S + 2SO_2(\uparrow) \\
Cu_2S + 2Cu_2O & 6Cu + SO_2(\uparrow)
\end{bmatrix}$ (Blister copper)

Refining of blister copper is done by poling followed by electrorefining but not by carbon reduction method.

28. The CORRECT statement(s) for cubic close packed (ccp) three dimensional structure is (are)

(A) The number of the nearest neighbours of an atom present in the topmost layer is 12

- (B) The efficiency of atom packing is 74%
- (C) The number of octahedral and tetrahedral voids per atom are 1 and 2, respectively
- (D) The unit cell edge length is $2\sqrt{2}$ times the radius of the atom

Ans. (B,C,D)

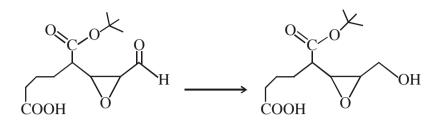
- Sol. CCP is ABC ABC type packing
 - (A) In topmost layer, each atom is in contact with 6 atoms in same layer and 3 atoms below this layer.

(B) Packing fraction =
$$\frac{4 \times \frac{4}{3} \pi r^3}{\left(\frac{4r}{\sqrt{2}}\right)^3} = (0.74)$$

(C) Each FCC unit has effective no of atoms = 4 Octahedral void = 4 Tetrahedral void = 8

(D) $4r = a\sqrt{2}$

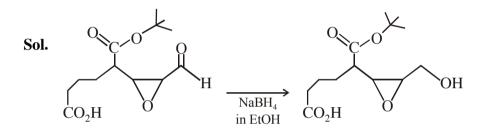
29. Reagent(s) which can be used to bring about the following transformation is(are)



(A) LiAlH_4 in $(\text{C}_2\text{H}_5)_2\text{O}$ (B) BH_3 in THF

(C) NaBH₄ in C₂H₅OH(D) Raney Ni / H₂ in THF

Ans. (C)



 $LiAlH_4$ in $(C_2H_5)_2O$; BH_3 in (THF); Raney Ni (H_2) either can reduce all functional group or can reduce some of the functional group of the compound given above in reactant side.

But NaBH₄ is example of selective reducing agent. It can not reduce -C-O- (ester group), -C-OH

(carboxylic acid group), \bigvee_{O} (epoxide group), but reduces -CH=O (aldehyde group) into -CH₂OH (1° alcohol)

- **30.** Mixture(s) showing positive deviation from Raoult's law at 35°C is (are)
 - (A) carbon tetrachloride + methanol (B) carbon disulphide + acetone
 - (C) benzene + toluene (D) phenol + aniline

Ans. (A, B)

- **Sol.** (A) H-bonding of methanol breaks when CCl_4 is added so bonds become weaker, resulting positive deviation.
 - (B) Mixing of polar and non-polar liquids will produce a solution of weaker interaction, resulting positive deviation

(C) Ideal solution

(D) -ve deviation because stronger H-bond is formed.

- **31.** The nitrogen containing compound produced in the reaction of HNO_3 with P_4O_{10}
 - (A) can also be prepared by reaction of P_4 and HNO_3
 - (B) is diamagnetic
 - (C) contains one N-N bond
 - (D) reacts with Na metal producing a brown gas

Sol. $P_4O_{10} + 4HNO_3 \xrightarrow{\text{dehydration of HNO}_3} 4(HPO_3) + 2N_2O_5$

(required product)

- (A) $P_4 + 20 \text{HNO}_3 \rightarrow 4\text{H}_3\text{PO}_4 + 20\text{NO}_2\uparrow + 4\text{H}_2\text{O}$
- (B) N_2O_5 is diamagnetic in nature

(C)
$$N_2O_5 \rightarrow O$$
 N_0 N_0

N₂O₅ contains one N–O–N bond not N–N bond.

- (D) Na + $N_2O_5 \rightarrow NaNO_3 + NO_2^{\uparrow}$ (Brown gas)
- 32. According to Molecular Orbital Theory,
 - (A) C_2^{2-} is expected to be diamagnetic
 - (B) O_2^{2+} is expected to have a longer bond length than O_2^{2-}
 - (C) N_2^+ and N_2^- have the same bond order
 - (D) He_2^+ has the same energy as two isolated He atoms

Ans. (A,C)

Sol (A) The molecular orbital energy configuration of C_2^{2-} is

 $\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2, \sigma_{2s}^{*2}, \pi_{2p_X}^2 = \pi_{2p_y}^2, \sigma_{2p_Z}^2$

In the MO of C_2^{2-} there is no unpaired electron hence it is diamagnatic

- (B) Bond order of O_2^{2+} is 3 and O_2 is 2 therefore bond length of O_2 is greater than O_2^{2+}
- (C) The molecular orbital energy configuration of N_2^+ is

$$\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2, \sigma_{2s}^{*2}, \pi_{2p_X}^2 = \pi_{2p_y}^2, \sigma_{2p_Z}^1$$

Bond order of
$$N_2^+ = \frac{1}{2}(9-4)$$

The molecular orbital energy configuration of N_2^- is

$$\sigma_{1s}^2, \sigma_{1s}^{*2}, \sigma_{2s}^2, \sigma_{2s}^{*2}, \pi_{2p_X}^2 = \pi_{2p_y}^2, \sigma_{2p_Z}^2, \pi_{2p_X}^{*1} = \pi_{2p_y}^*$$

Bond order of $N_2^- = \frac{1}{2}(10-5)$ = 2.5

(D) He_2^+ has less energy as compare to two isolated He atoms

SECTION-3 : (Maximum Marks : 12)

- This section contains **TWO** paragraphs.
- Based on each paragraph, there are **TWO** questions.
- Each question has **FOUR** options (A), (B), (C) and (D) **ONLY ONE** of these four options is correct.
- For each question, darken the bubble corresponding to the correct option in the ORS.
- For each question, marks will be awarded in <u>one of the following categories</u> :

Full Marks : +3 If only the bubble corresponding to the correct answer is darkened.

Zero Marks : 0 In all other cases.

PARAGRAPH 1

Thermal decomposition of gaseous X_2 to gaseous X at 298 K takes place according to the following equation :

$$X_2(g) \implies 2X(g)$$

The standard reaction Gibbs energy, $\Delta_r G^\circ$, of this reaction is positive. At the start of the reaction, there is one mole of X_2 and no X. As the reaction proceeds, the number of moles of X formed is given by β . Thus, $\beta_{equilibrium}$ is the number of moles of X formed at equilibrium. The reaction is carried out at a constant total pressure of 2 bar. Consider the gases to behave ideally.

(Given : $R = 0.083 \text{ L bar } \text{K}^{-1} \text{ mol}^{-1}$)

33. The equilibrium constant K_p for this reaction at 298 K, in terms of $\beta_{equilibrium}$, is

(A)
$$\frac{8\beta_{equilibrium}^2}{2-\beta_{equilibrium}}$$
 (B) $\frac{8\beta_{equilibrium}^2}{4-\beta_{equilibrium}^2}$ (C) $\frac{4\beta_{equilibrium}^2}{2-\beta_{equilibrium}}$ (D) $\frac{4\beta_{equilibrium}^2}{4-\beta_{equilibrium}^2}$

Ans. (B)

Sol. $X_2(g) \implies 2X(g)$

n

$$1 - \frac{p_{eq.}}{2} \qquad \beta_{eq.}$$

$$K_{p} = \frac{P_{x}^{2}}{P_{x_{2}}} = \frac{\left(\frac{\beta_{eq.}}{1 + \frac{\beta_{eq}}{2}}P_{T}\right)^{2}}{\left(\frac{1 - \frac{\beta_{eq.}}{2}}{1 + \frac{\beta_{eq}}{2}}P_{T}\right)}$$

$$K_{p} = \frac{\beta_{eq.}^{2}}{1 - \frac{\beta_{eq.}^{2}}{4}}P_{T} = \frac{2\beta_{eq}^{2}}{1 - \frac{\beta_{eq.}}{4}}$$

$$= \frac{8\beta_{eq.}^{2}}{4 - \beta_{eq.}^{2}}$$

34. The INCORRECT statement among the following, for this reaction, is

- (A) Decrease in the total pressure will result in formation of more moles of gaseous X
- (B) At the start of the reaction, dissociation of gaseous X₂ takes place spontaneously
- (C) $\beta_{\text{equilibrium}} = 0.7$

(D)
$$K_c < 1$$

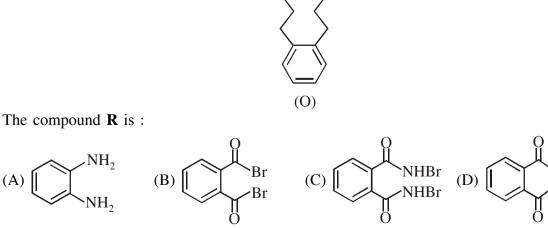
Ans. (C)

Sol. (A) On decreasing $P_T \left[Q = \frac{n_{x^2} P_T}{n_{x_2} n_T} \right] Q$ will be less than Kp reaction will move in forward direction

(B) At the start of the reaction $\Delta G = \Delta G^0 + RT \ln Q$ t = 0, $Q = 0 \Rightarrow \Delta_{rxn}G = -ve$ (spontaneous) (C) if $\beta_{eq} = 0.7$ $K_p = \frac{8 \times 0.49}{4 - 0.49} = \frac{3.92}{3.51}$ $K_p > 1$ Since it is given that $\Delta G^0 > 0 \Rightarrow K_p < 1$ \therefore This is incorrect (D) $K_p = K_C \times (RT)^{\Delta n_g}$ $K_C = \frac{K_p}{(R \times 298)^1}$ $K_C < 1$

PARAGRAPH 2

Treatment of compound **O** with $KMnO_4 / H^+$ gave **P**, which on heating with ammonia gave **Q**. The compound **Q** on treatment with $Br_2 / NaOH$ produced **R**. On strong heating, **Q** gave **S**, which on further treatmenet with ethyl 2-bromopropanoate in the presence of KOH following by acidification, gave a compound **T**.



Ans. (A)

35.

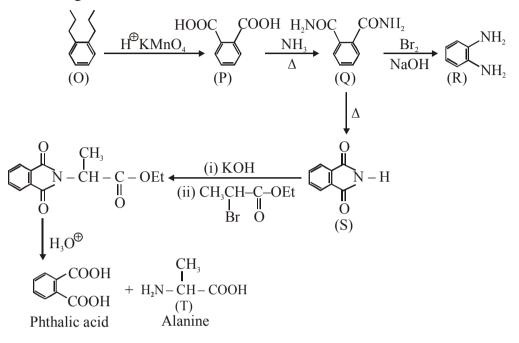
JBr

36. The compound **T** is :

(A) Glycine (B) Alanine (C) Valine (D) Serine **Ans. (B)**

Sol.

Solution Q.35 & 36.



 ${\bf Q}$ to ${\bf R}$ is Hoffmann's bromamide degradation reaction

S to T is Gabriel's phthalimide sysnthesis