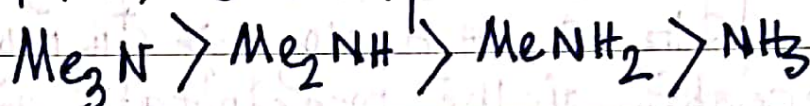


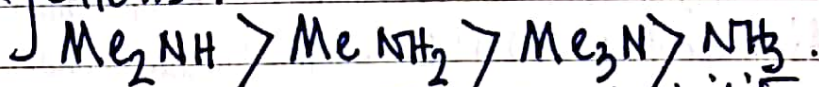
ALIPHATIC AMINES - SOME REACTIONS

(i) **Basicity**: In gaseous phase or in non-polar solvents, e^- density on the N atom dictates the feasibility of its donation to a Lewis acid and hence determines basicity. Alkyl groups enhance the e^- density on the amino N by +I effect. Hence, more alkyl groups imply more basicity.

Then, basicity order is

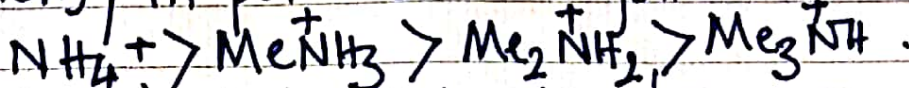


In some cases it has been observed that a steric factor operates upon protonation or alkylation of the 3° amine; consequently, the third alkyl group reduces the basicity. The order follows:

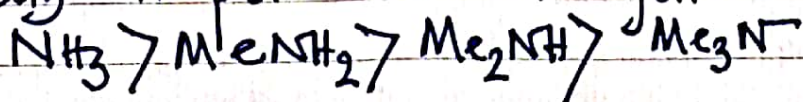


In polar solvents, eg. water, stability due to solvation of the conjugate acid cation dominates. More the charge density on the conjugate acid, better the solvation, more the solvation energy, more the basicity.

Solvation energy in polar solvents follows the order:



Hence basicity in polar solvents follows the order:



25

Tuesday

Feb 2020  Week-9 (056-310)

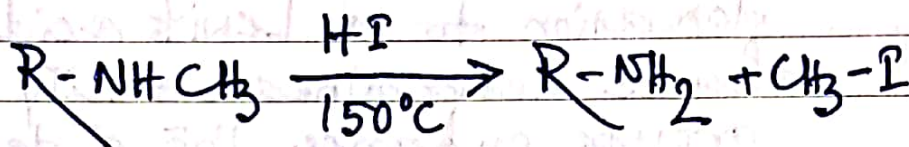
February

2020

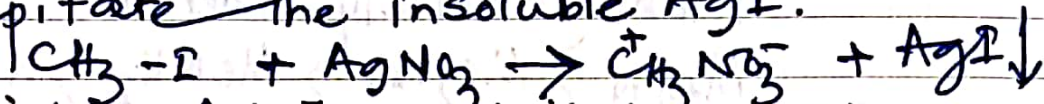
S	M	T	W	T	F	S	S	M	T	W	T	F	S
						1	2	3	4	5	6	7	8
9	10	11	12	13	14	15	16	17	18	19	20	21	22
23	24	25	26	27	28	29	.	.	.	.	.	.	.

(iv) The Herzig-Meyer reaction - Quantitative estimation of methylamino group:

At 150°C , HI transforms N-methyl moieties to methyl iodide:



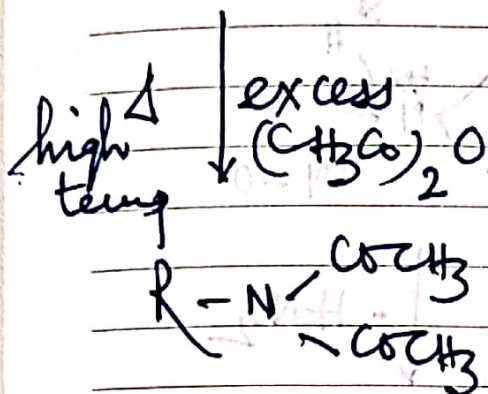
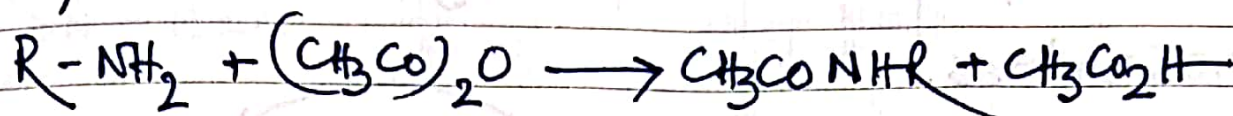
This forms the basis of quantitative estimation of methylamino function. The methyl iodide so generated is run into AgNO_3 solution to precipitate the insoluble AgI .



The weight of the precipitate allows for gravimetric estimation of methylamino group.

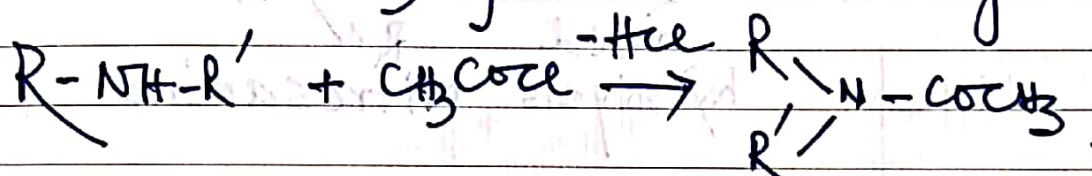
The same reaction may be utilized for estimation of methoxyl function; in this case, the reaction temperature is sufficiently 100°C .

(iii) Acylation:



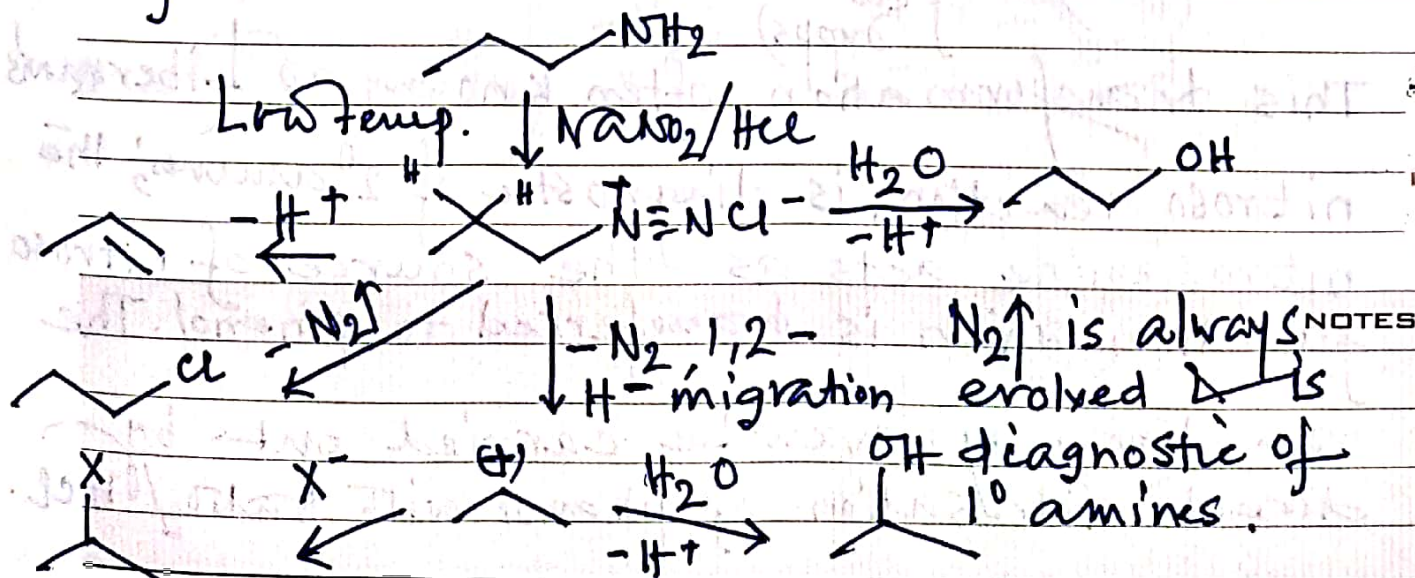
The monoacetyl derivatives are well defined crystalline solids and are often capable of diagnosing the parent amines.

2° amines only form the monoacyl derivative.



(iv) Nitrosations:

A 1° amine, on treatment with nitrous acid, generates the alkyl diazonium cation which can undergo a complicated set of reactions:



27

Thursday

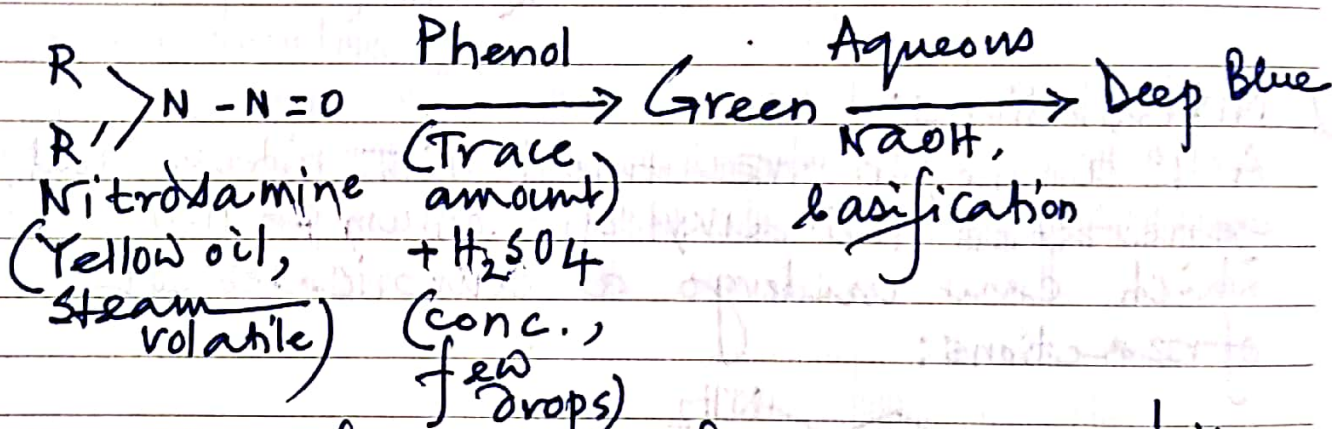
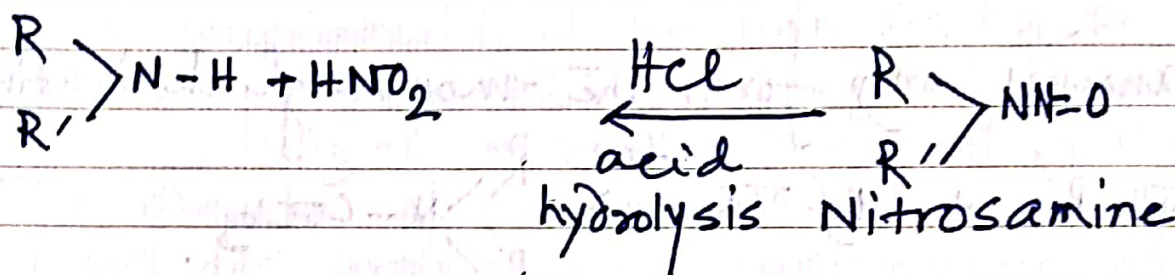
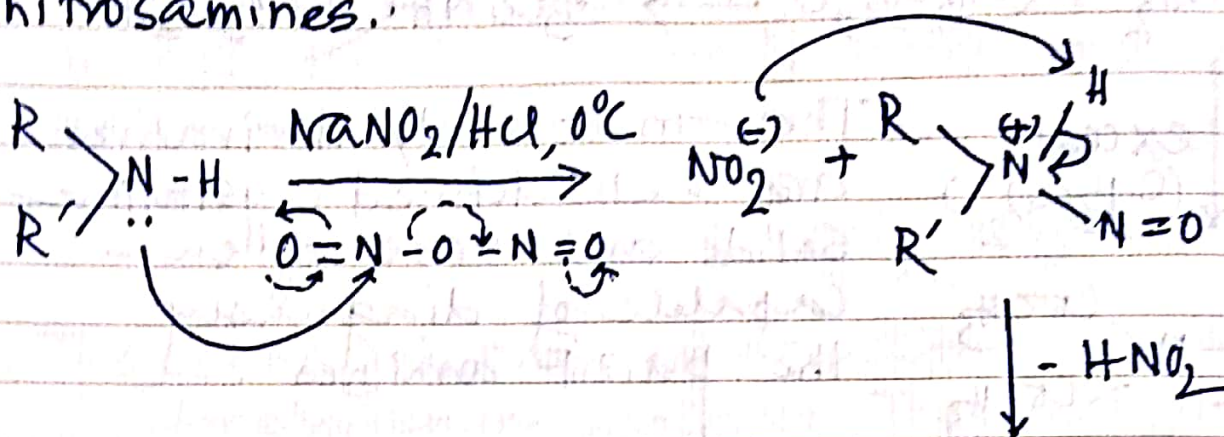
Feb 2020 Week-9 (058-308)

February

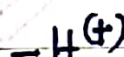
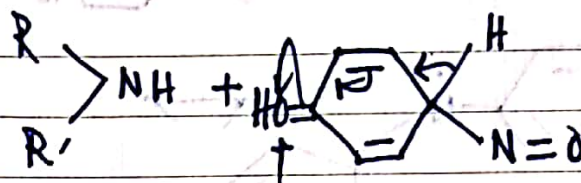
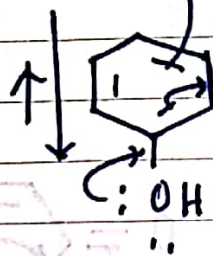
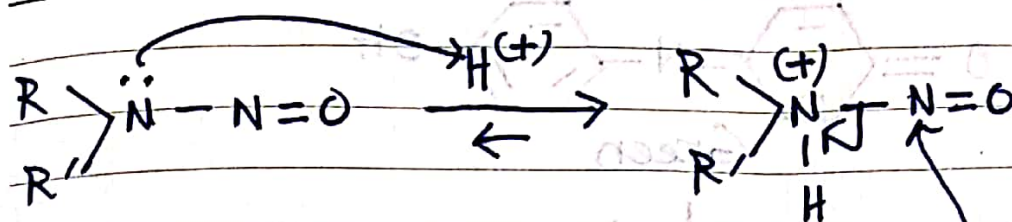
2020

S	M	T	W	T	F	S	S	M	T	W	T	F	S
						1	2	3	4	5	6	7	8
9	10	11	12	13	14	15	16	17	18	19	20	21	22
23	24	25	26	27	28	29	.	.	.	.	.	.	.

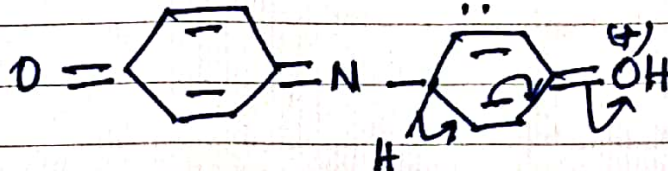
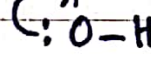
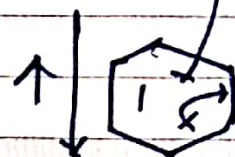
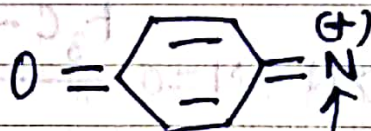
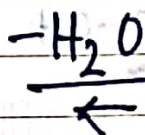
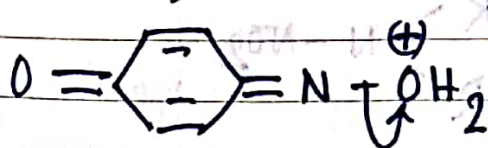
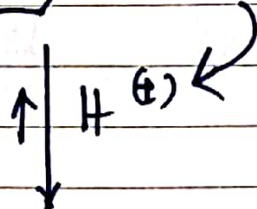
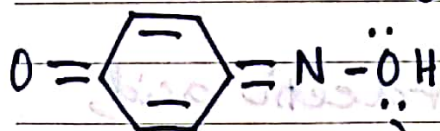
2° amines, upon nitrosation, generate nitrosamines.



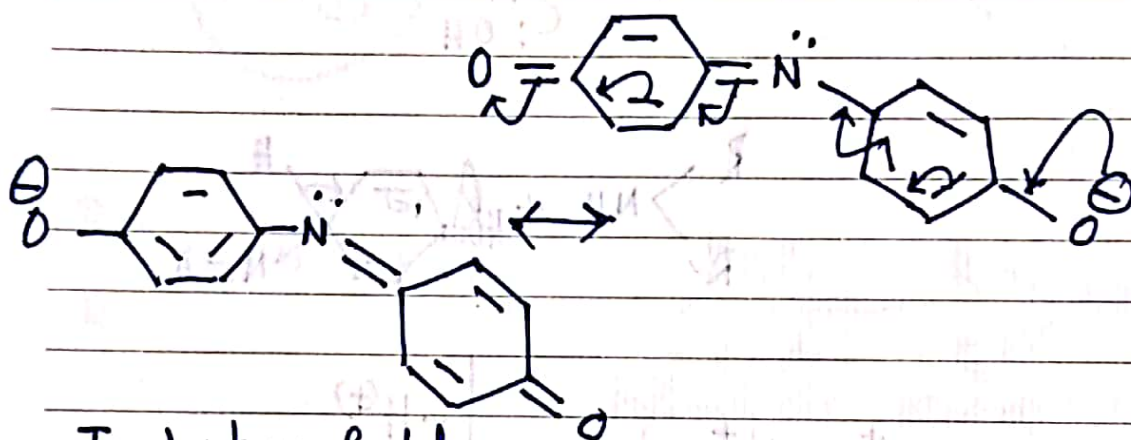
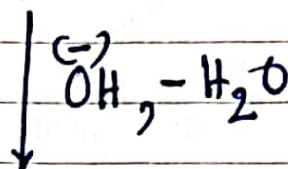
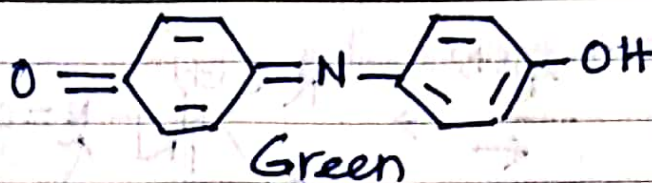
NOTES
This transformation, often known as Libermann's nitroso reaction, is diagnostic of 2° amines; the nitrosamine acts as the source of nitroso function which is transferred to phenol. The reaction may even be carried out by direct nitrosation of phenol with NaNO₂/HCl.



$-\text{H}^+, +\text{H}^+$
tautomerise



aromatization $\longrightarrow$

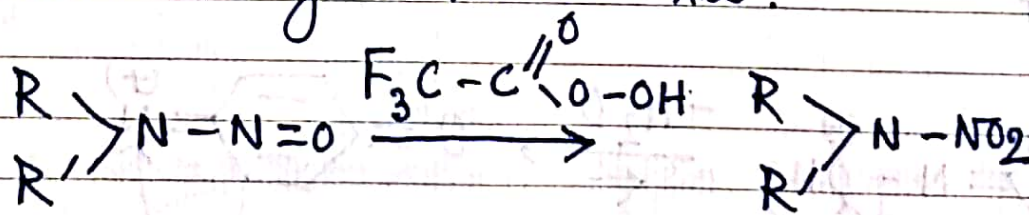


Indophenol blue

Upon oxidation with trifluoroperacetic acid,

01 SUNDAY

nitrosamines give nitramines.



NOTES

