

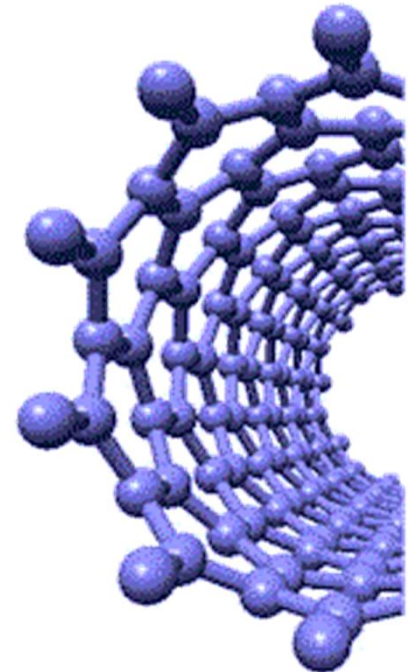


INVESTMENTS IN EDUCATION DEVELOPMENT

Innovation and Development of Study Field Nanomaterials at the Technical University of Liberec

nano.tul.cz

These materials have been developed within the ESF project: Innovation and development of study field Nanomaterials at the Technical University of Liberec



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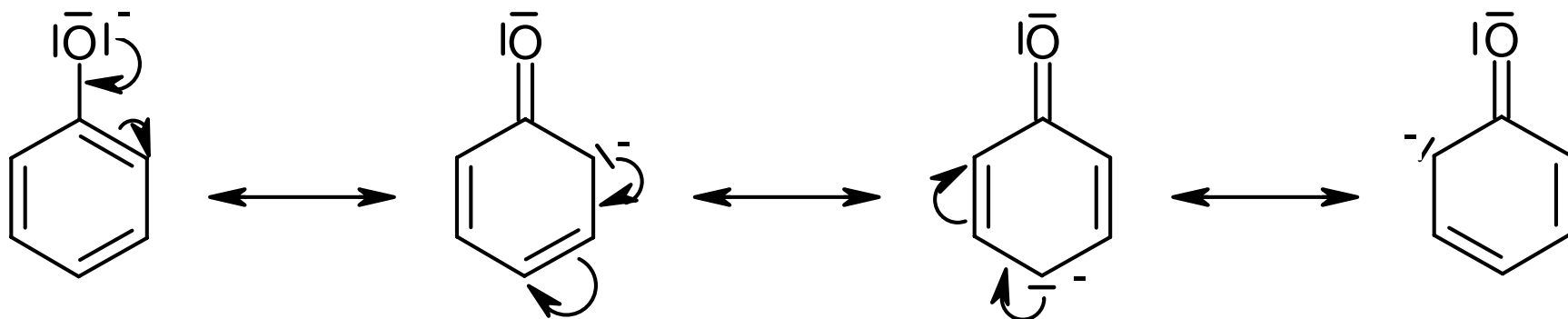




Organic Chemistry I – Chapter 14



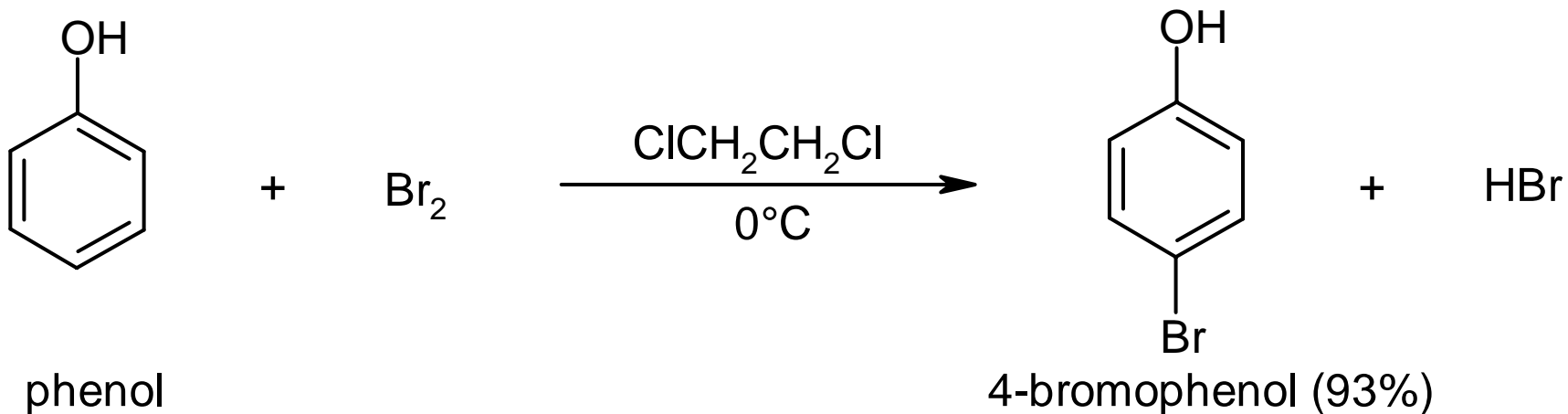
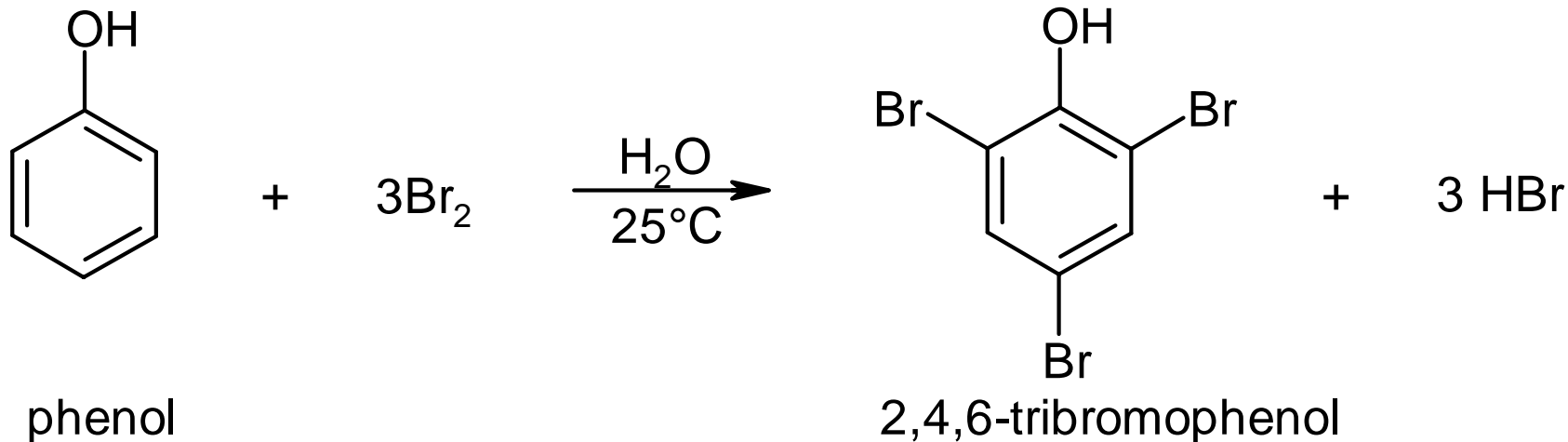
Phenols – acidity – stabilisation of anion by resonance



Compounds	pK _a	Compounds	pK _a
Phenol	10,0	3-nitrophenol	8,4
2-methylphenol	10,3	4-nitrophenol	7,2
3-methylphenol	10,1	2,4-dinitrophenol	4,0
4-methylphenol	10,3	3,5-dinitrophenol	6,7
2-nitrophenol	7,2	2,4,6-trinitrophenol	0,4



Phenols – are extremely reactive aromatics

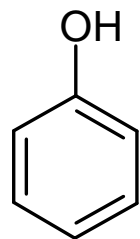




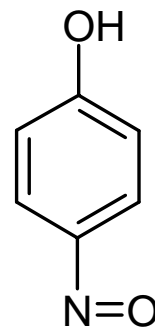
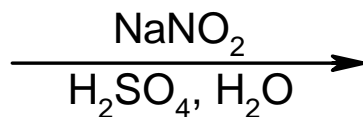
Organic Chemistry – chemistry of aromatics



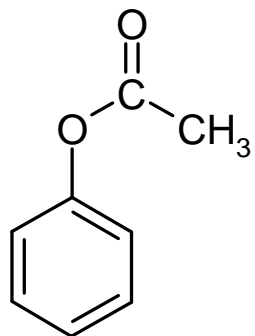
Phenols – are extremely reactive aromatics



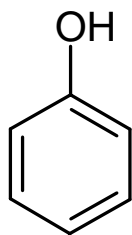
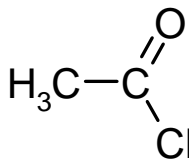
phenol



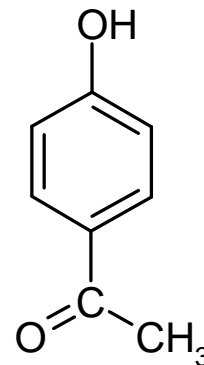
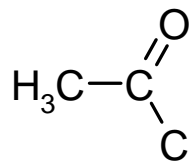
4-nitrosophenol



phenyl-acetate

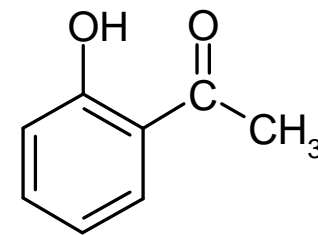


phenol



4-hydroxyaceto-
phenone (74%)

+



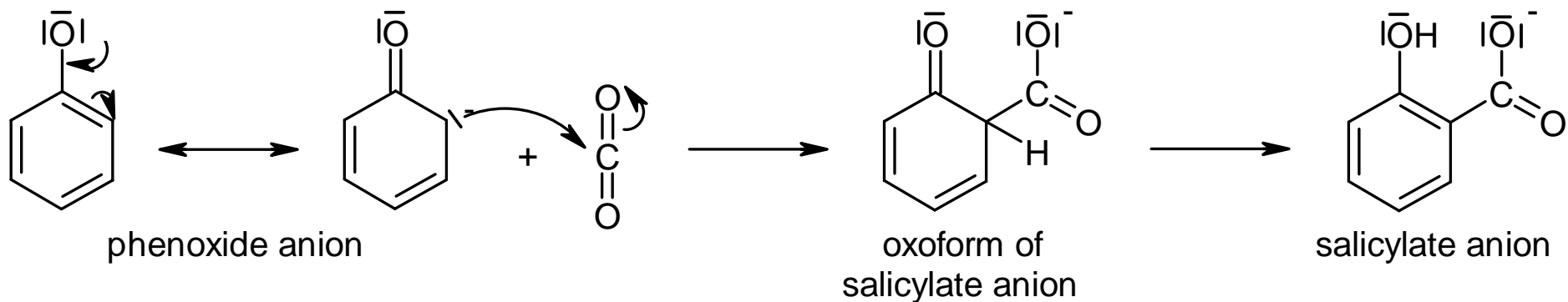
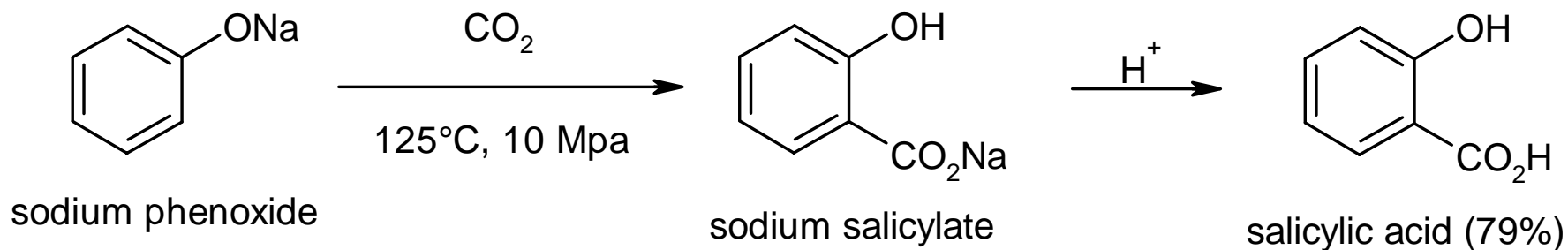
2-hydroxyaceto-
phenone (16%)



Organic Chemistry – chemistry of aromatics

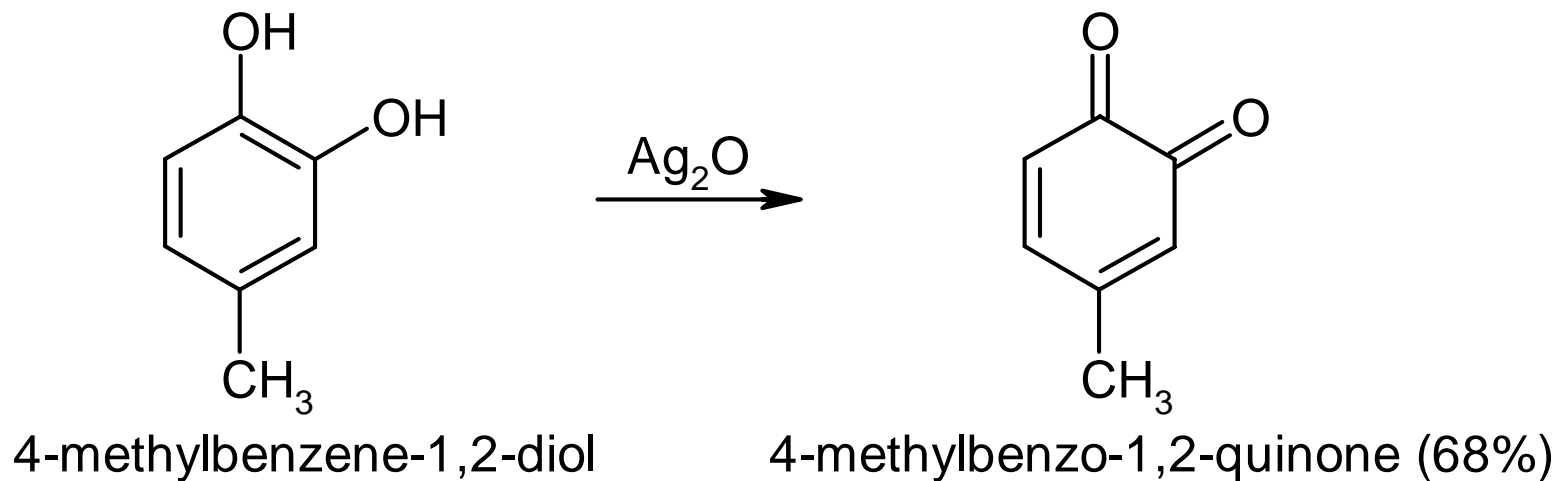
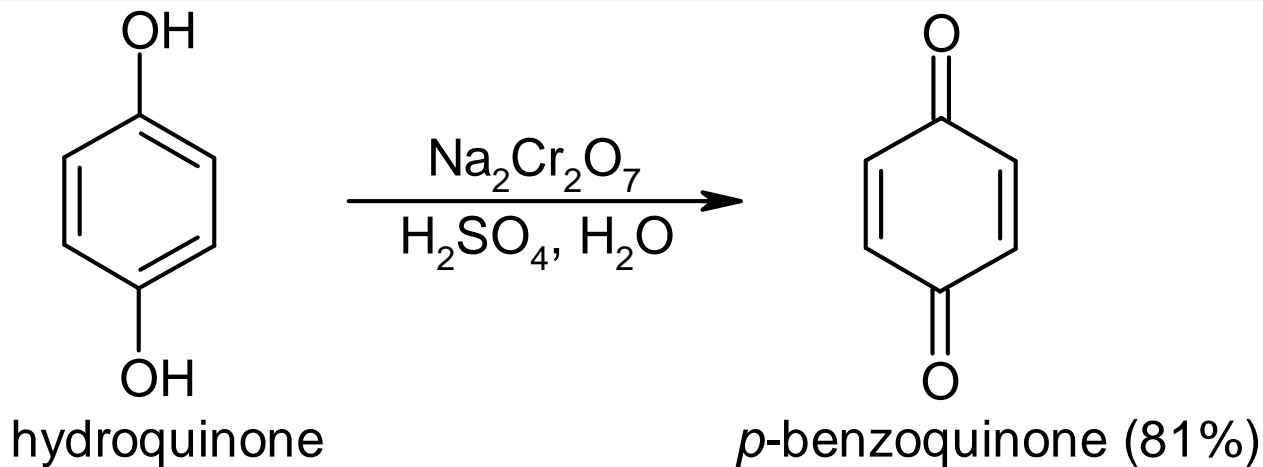


Phenols – are extremely reactive aromatics





Phenols – oxidation to quinones

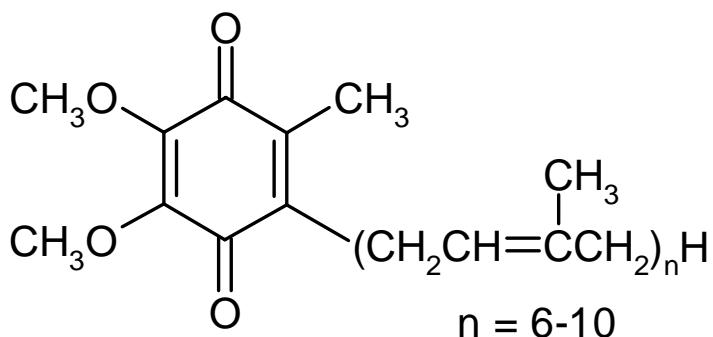




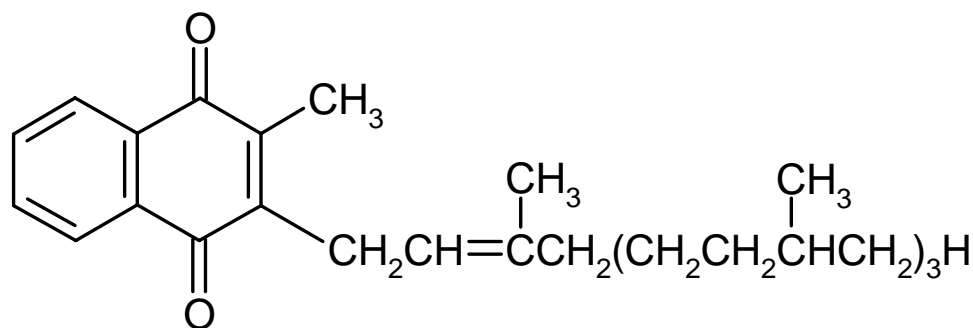
Organic Chemistry – chemistry of aromatics



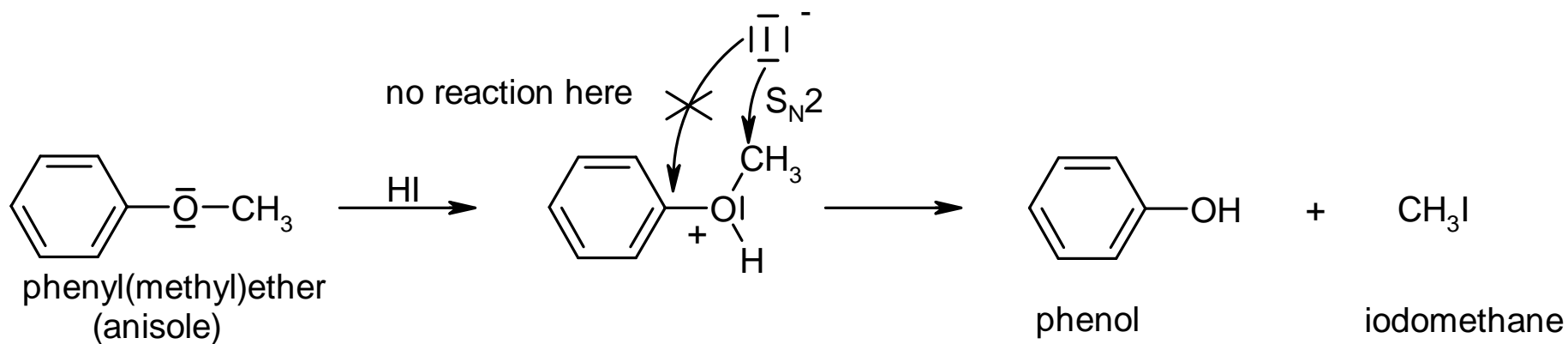
Phenols – oxidation to quinones and cleavage of ethers



ubiquinone (coenzyme Q)

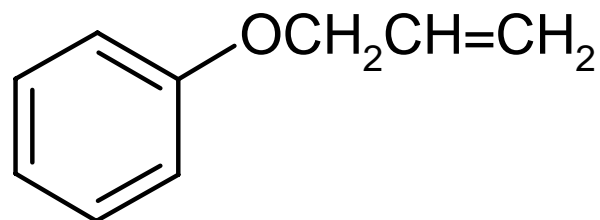


vitamine K

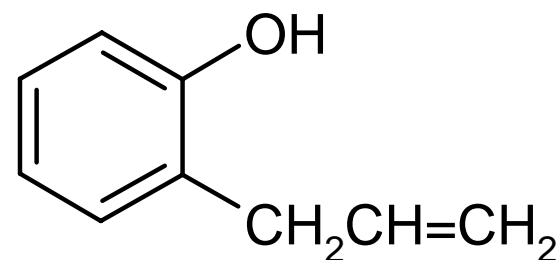
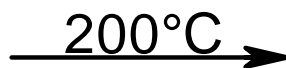




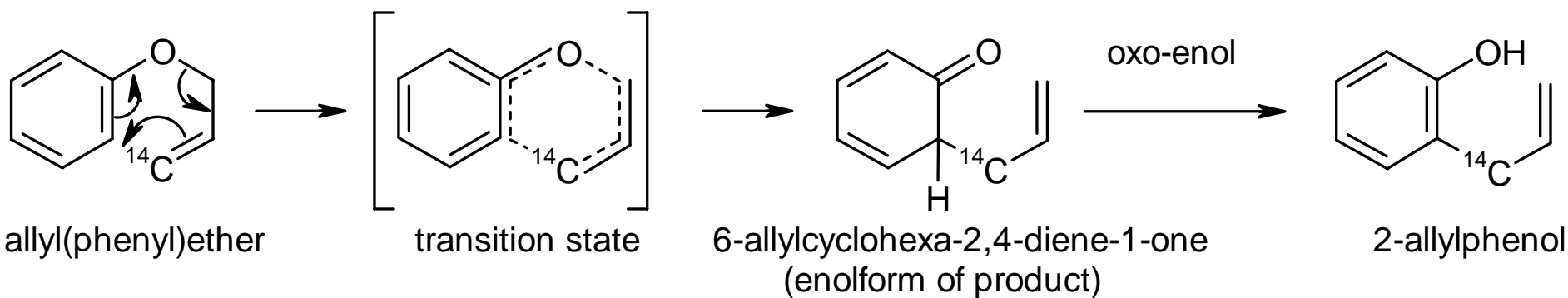
Phenols – Claisen rearrangement of allylarylethers



allyl(phenyl)ether



2-allylphenol (75%)

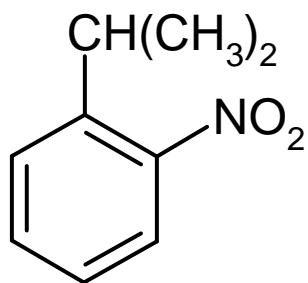
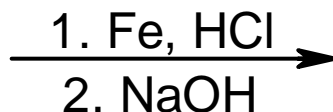
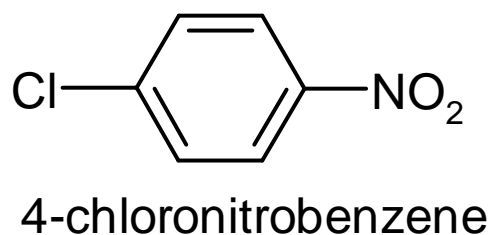
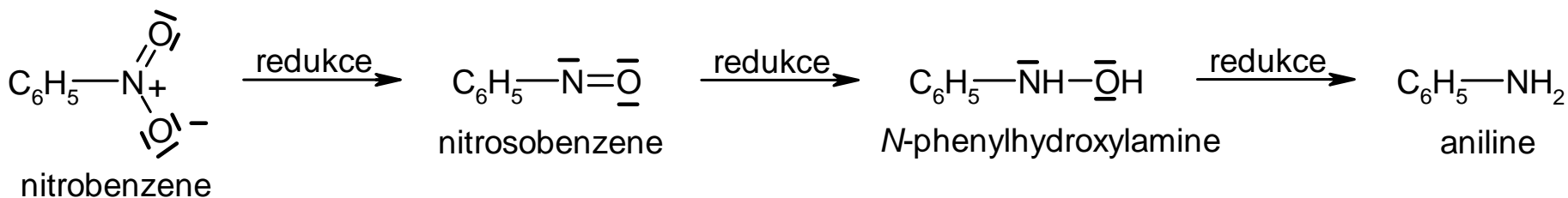




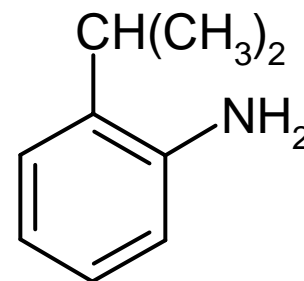
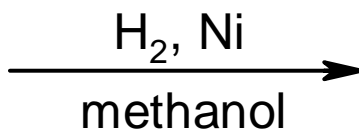
Organic Chemistry – chemistry of aromatics



Aromatic amines – preparation –reduction of nitrocompounds



2-isopropyl-1-nitrobenzene



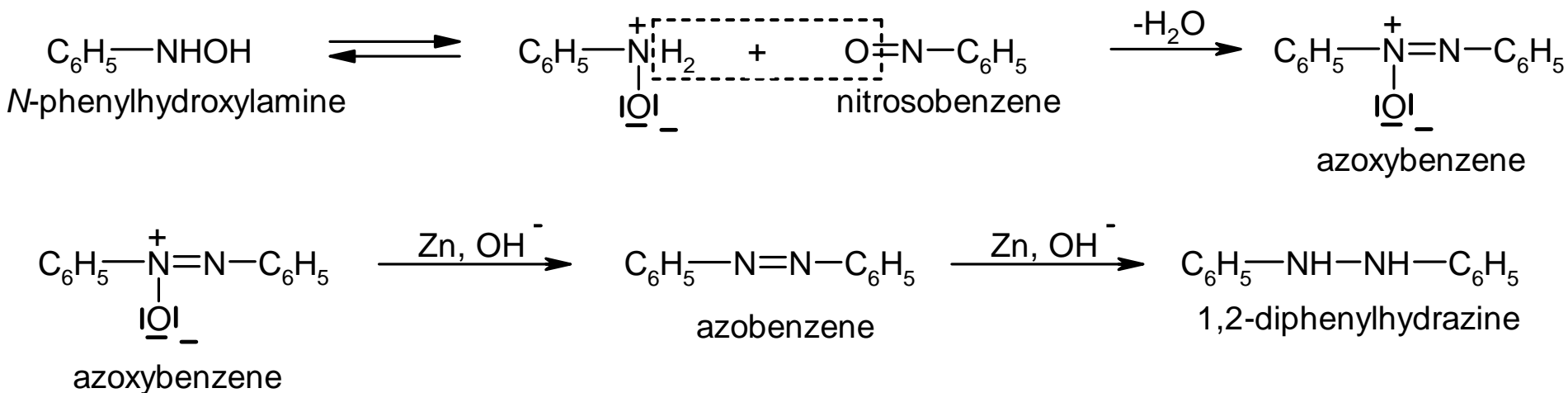
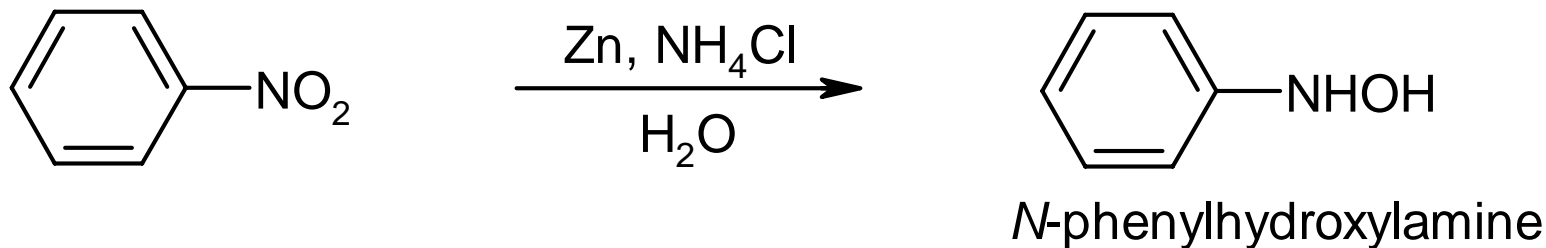
2-isopropylaniline (92%)



Organic Chemistry – chemistry of aromatics

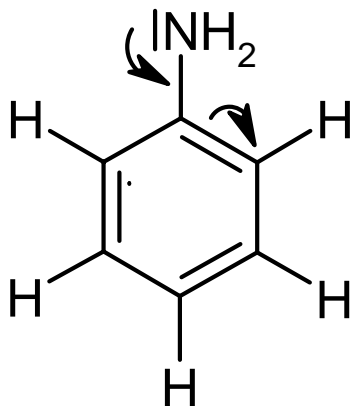


Aromatic amines – preparation – reduction of nitrocompounds

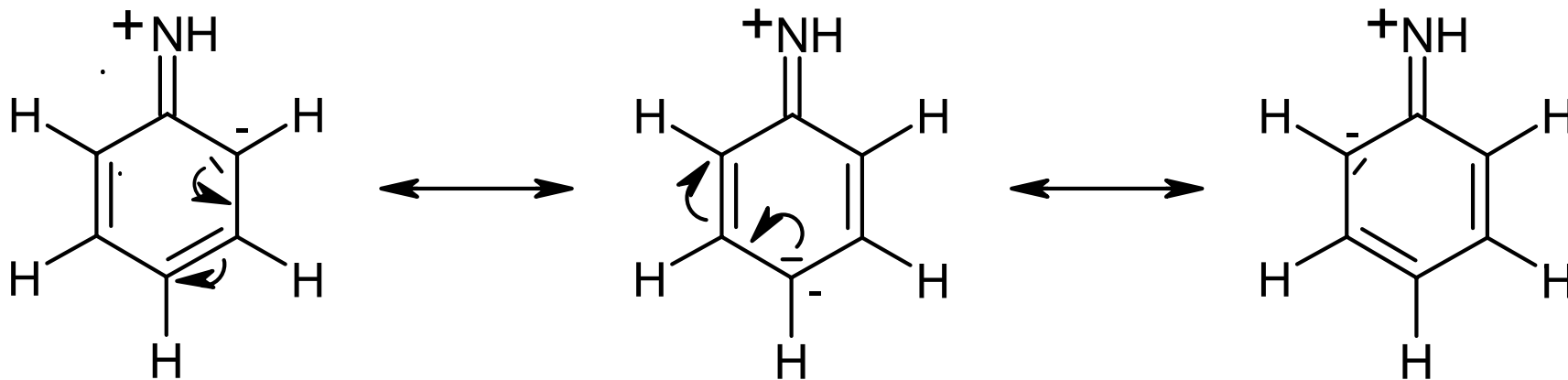




Aromatic amines - structure

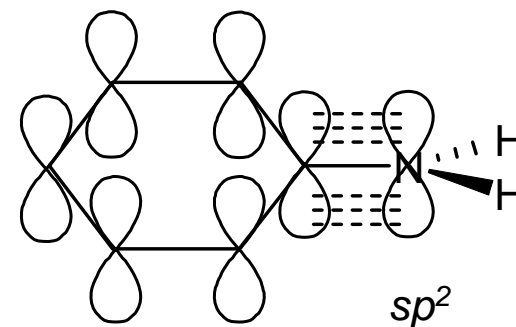
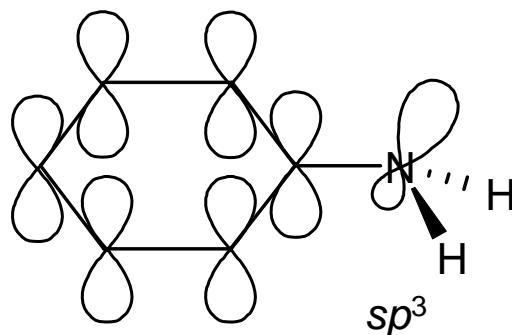
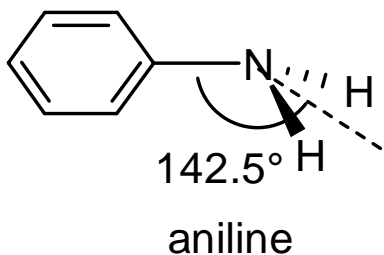


aniline
benzenamine
aminobenzene
phenylamine

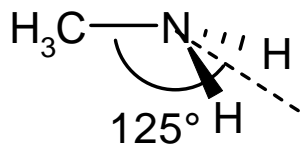




Aromatic amines - structure



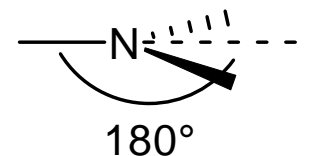
aniline - conjugation of nonbonded electrons



methylamine



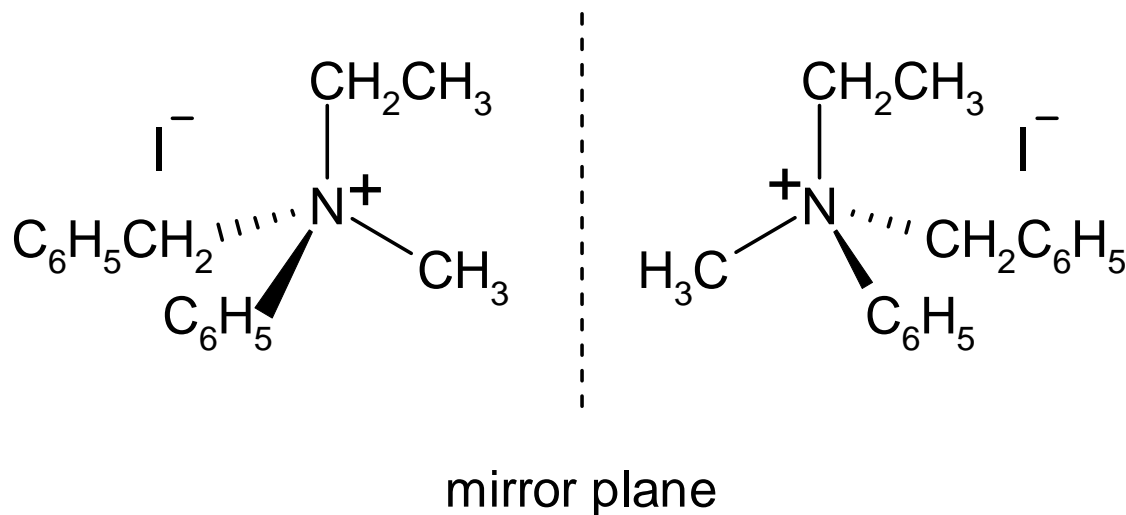
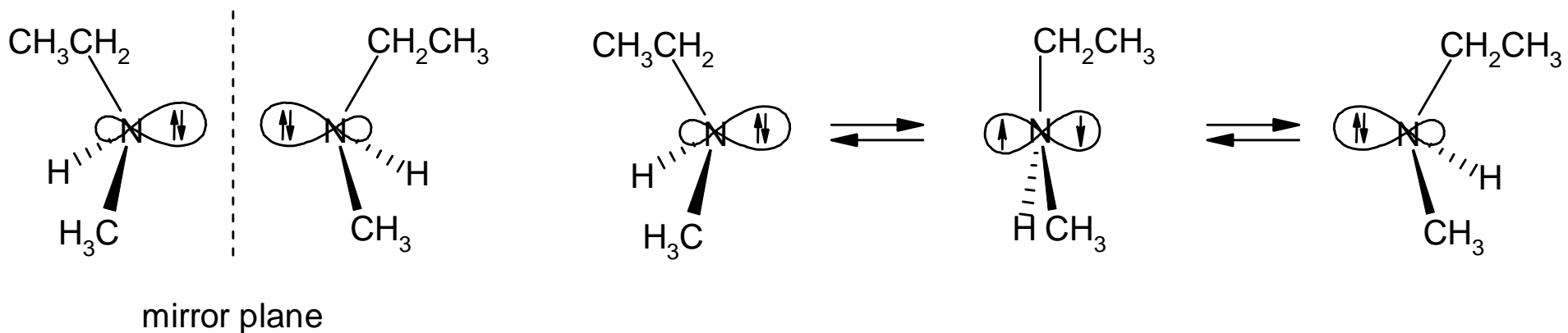
sp^3 hybridisation on N



sp^2 hybridisation on N



Aromatic amines – structure, chirality

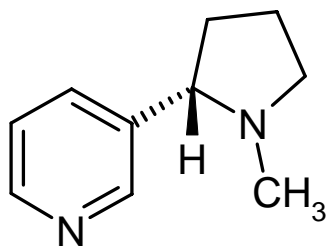




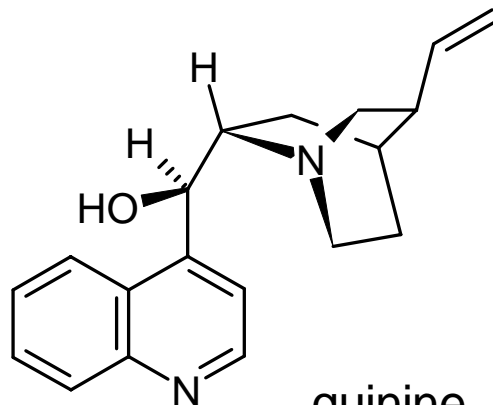
Organic Chemistry – chemistry of aromatics



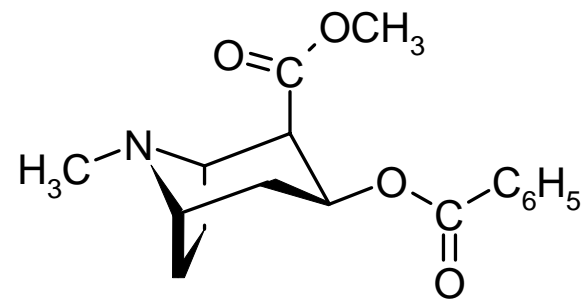
Amines – natural compounds



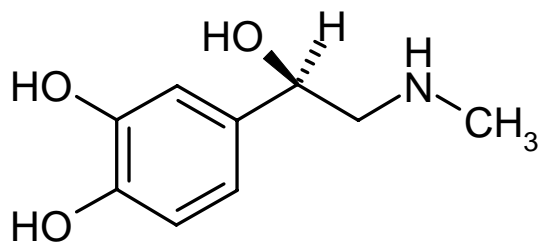
nicotine



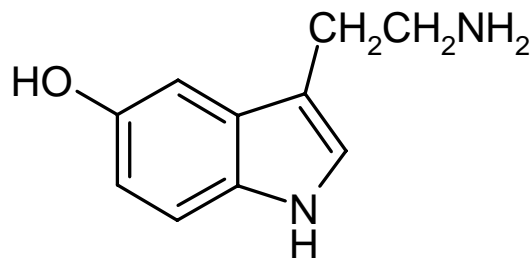
quinine



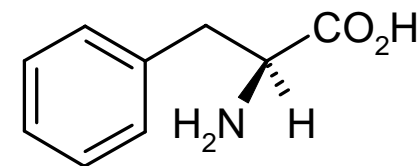
cocaine



adrenaline



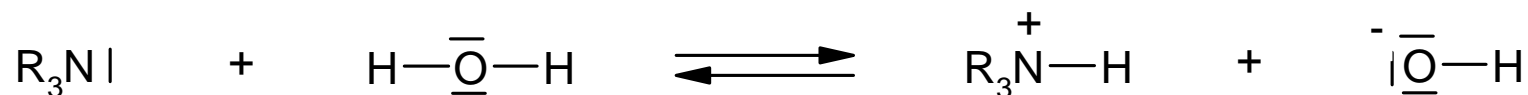
serotonin



L-phenylalanine



Amines – basicity



$$K_b = \frac{[\text{R}_3\text{NH}^+][\text{OH}^-]}{[\text{R}_3\text{N}]} \quad \text{p}K_b = -\log K_b$$

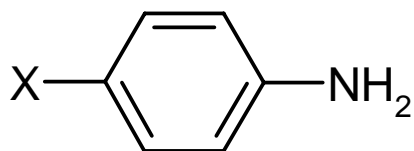
Amine	p <i>K</i> _b	Amine	p <i>K</i> _b
amoniak	4,7	secondary amines	
primary amines		(CH ₃) ₂ NH	3,3
CH ₃ NH ₂	3,4	(CH ₃ CH ₂)NH	2,9
CH ₃ CH ₂ NH ₂	3,2	C ₆ H ₅ NHCH ₃	9,2
(CH ₃) ₂ CHNH ₂	3,4	Tertiary amines	
(CH ₃) ₃ CNH ₂	3,6	(CH ₃) ₃ N	4,3
C ₆ H ₅ NH ₂	9,4	(CH ₃ CH ₂) ₃ N	3,2
		C ₆ H ₅ N(CH ₃) ₂	8,9



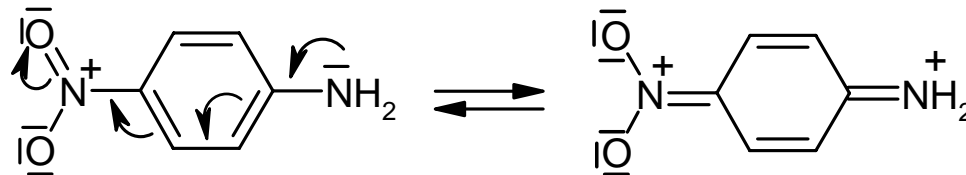
Organic Chemistry – chemistry of aromatics



Aromatic amines – basicity – role of substituent



X	pK_b
H	9,4
CH ₃	8,7
CF ₃	11,5
O ₂ N	13,0

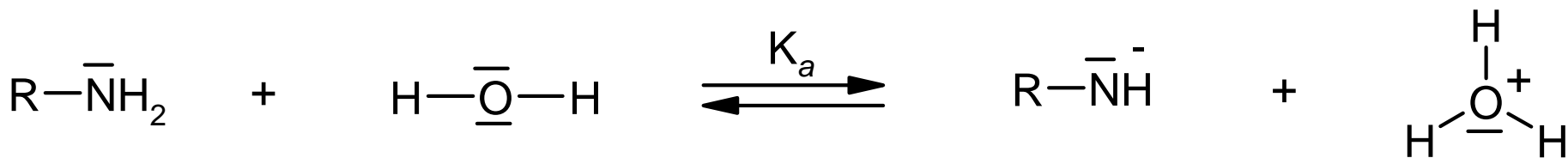




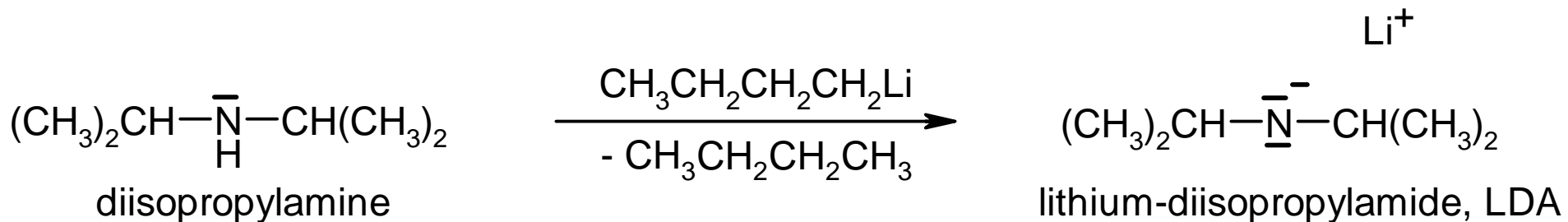
Organic Chemistry – chemistry of aromatics



Amines – as acids – deprotonation of them

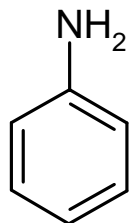


$$K_a = \frac{[\text{RNH}^-][\text{H}_3\text{O}^+]}{[\text{RNH}_2]} = \sim 10^{-35} \quad \text{p}K_a = -\log K_a = \sim 35$$

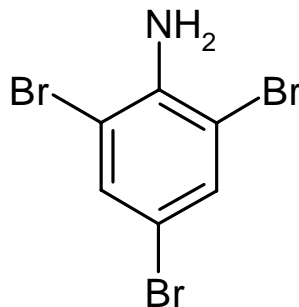
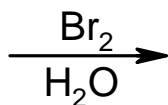




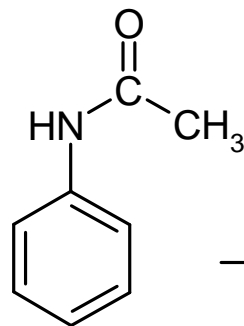
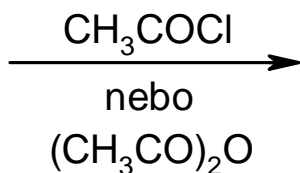
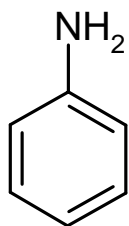
Aromatic amines – reactivity S_EAr



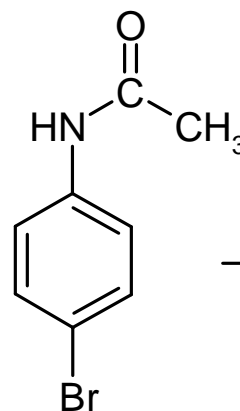
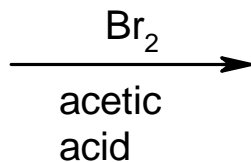
aniline



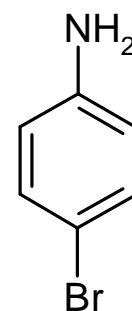
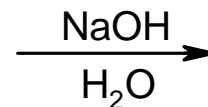
2,4,6-tribromoaniline (quantitative)



acetanilide



4-bromoacetanilide
(main product)



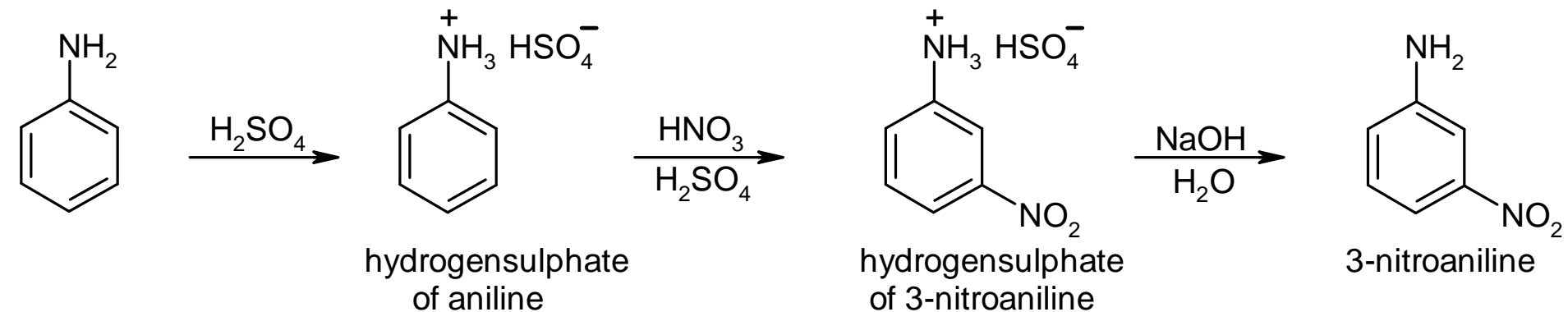
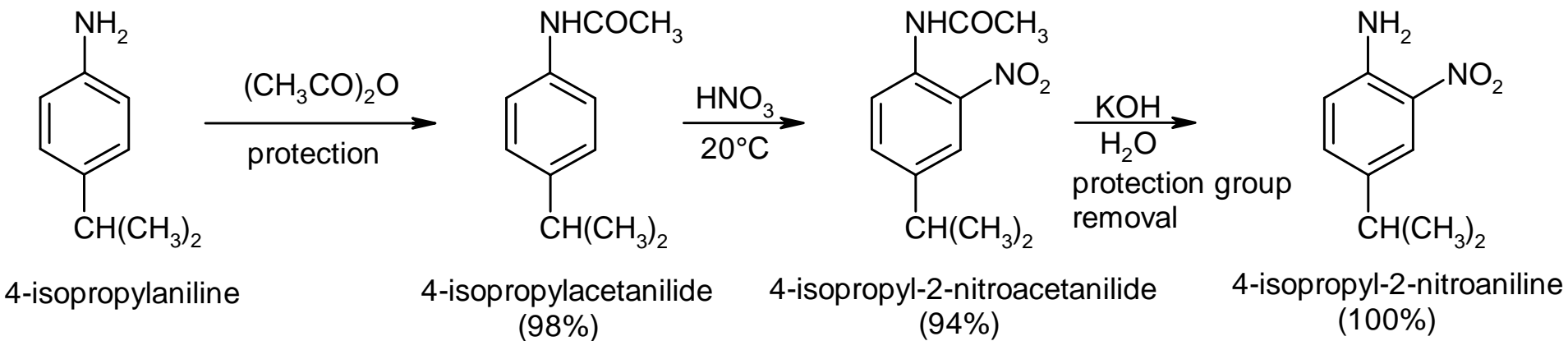
4-bromoaniline



Organic Chemistry – chemistry of aromatics



Aromatic amines – reactivity S_EAr

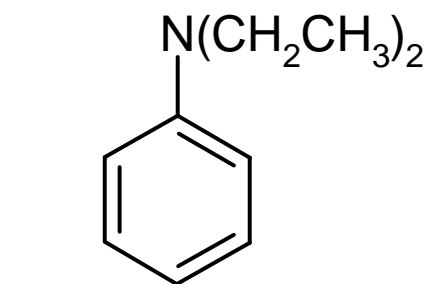
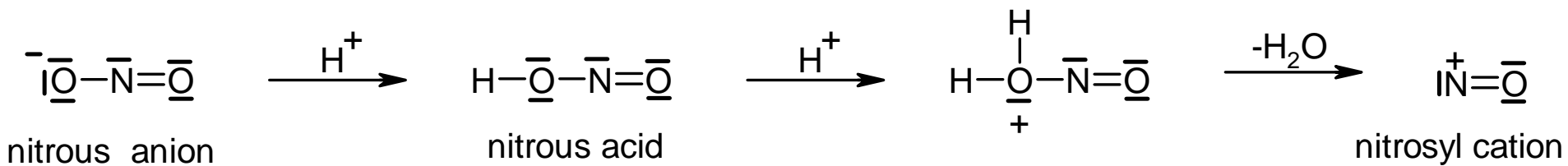




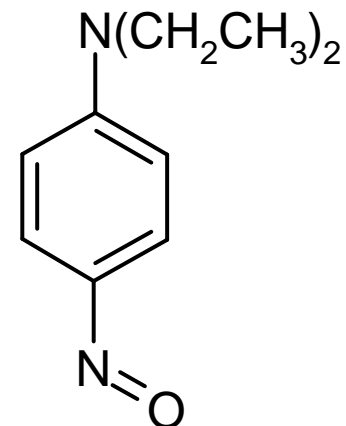
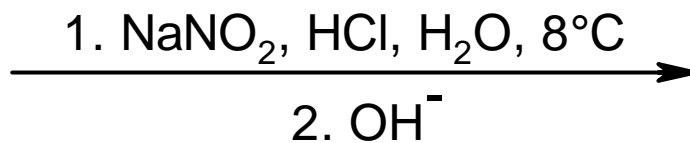
Organic Chemistry – chemistry of aromatics



Aromatic amines – reactivity S_EAr



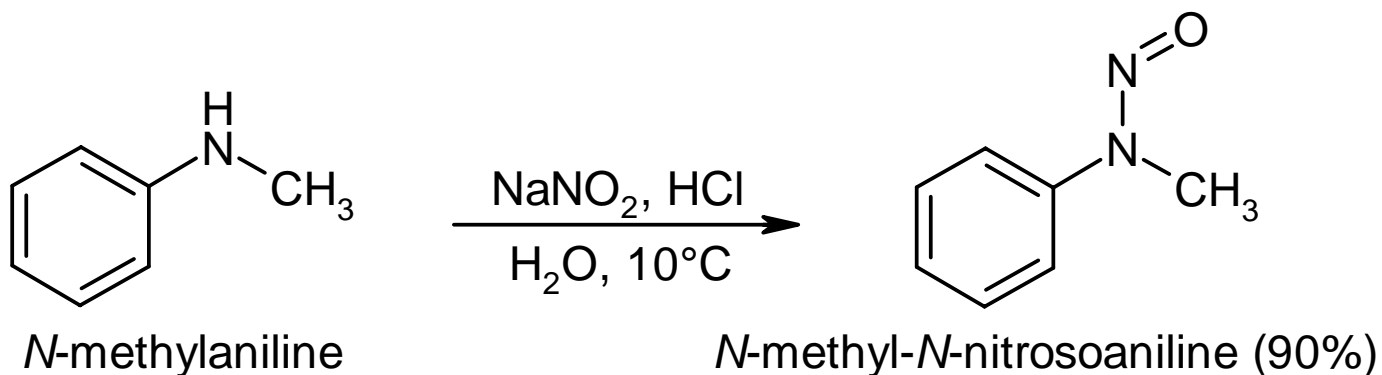
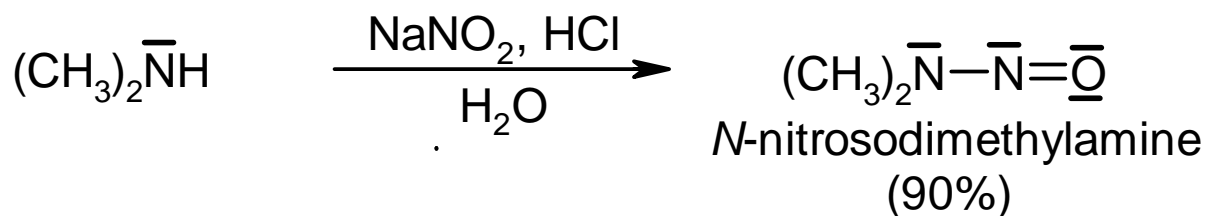
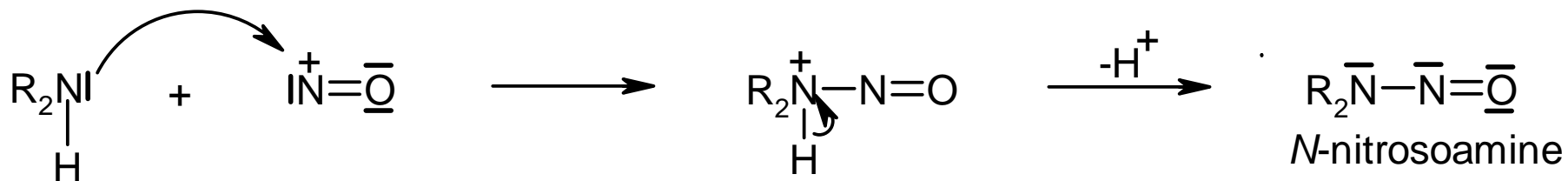
N,N-diethylaniline



N,N-diethyl-4-nitrosoaniline (95%)



Aromatic amines – reactivity S_EAr

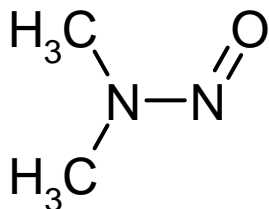




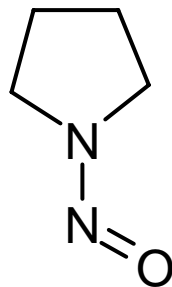
Organic Chemistry – chemistry of aromatics



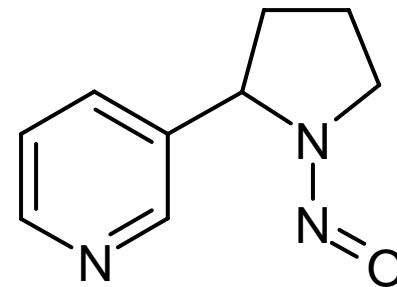
Aromatic amines – reactivity S_EAr



N-nitrosodimethylamine
(found e.g. in beer)



N-nitrosopyrrolidine
(in roasted beans)



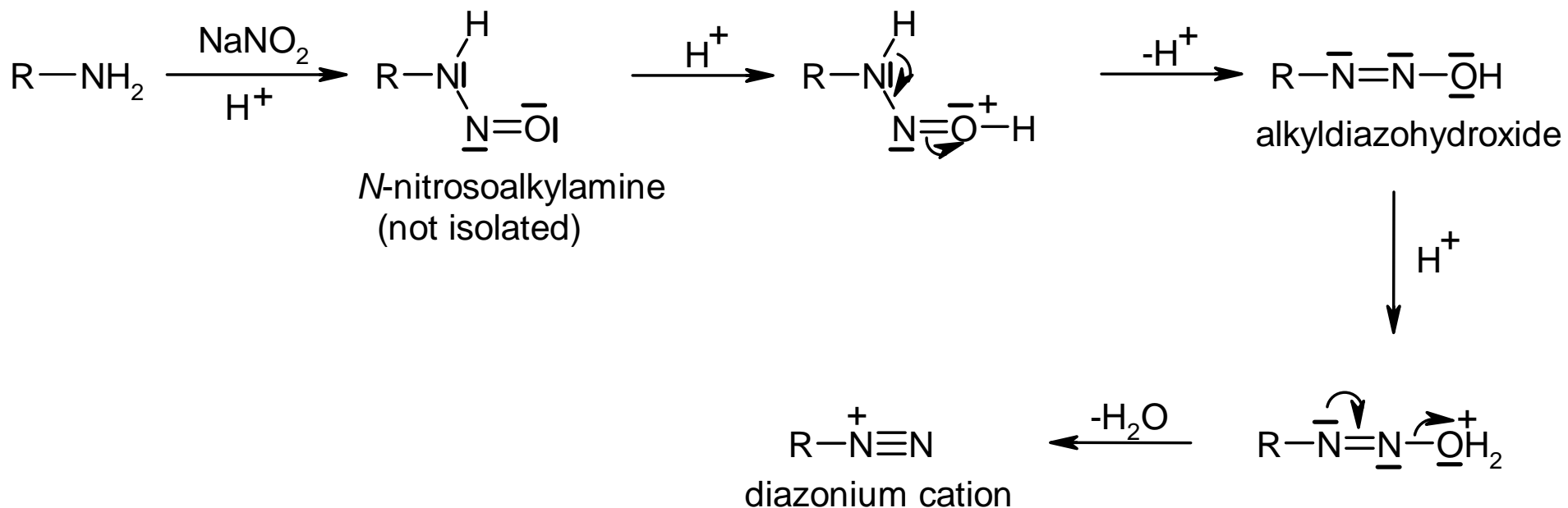
N-nitrosonornicotine
(in tobacco smoke)



Organic Chemistry – chemistry of aromatics

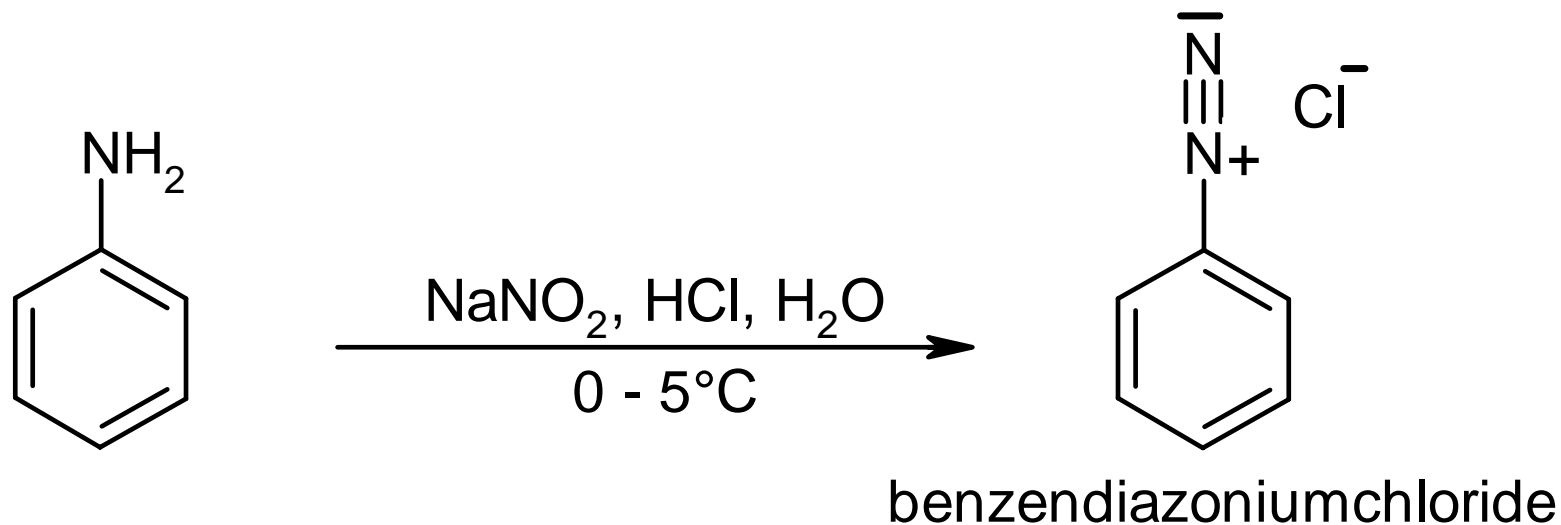
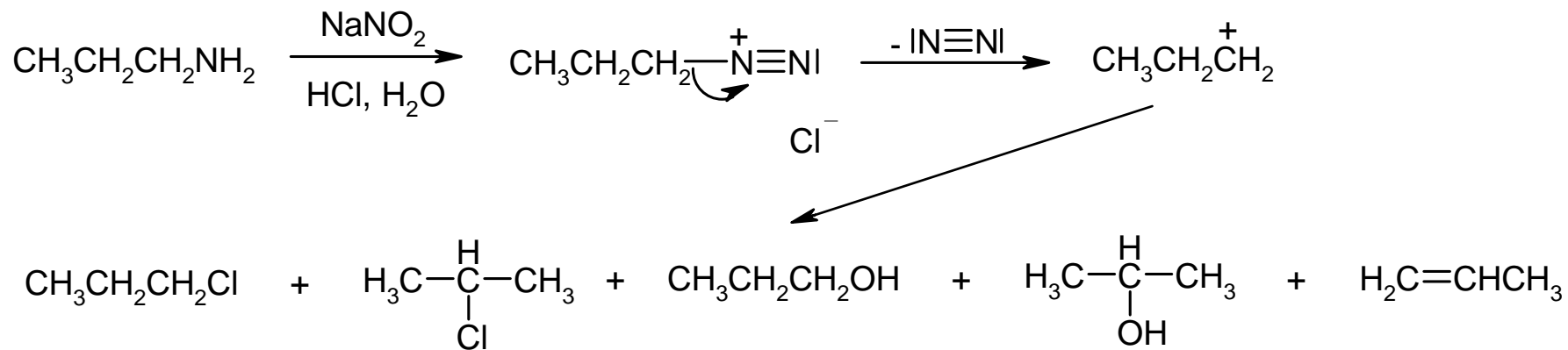


Amines – reactivity – diazonium salt formation





Amines – reactivity – diazonium salt formation

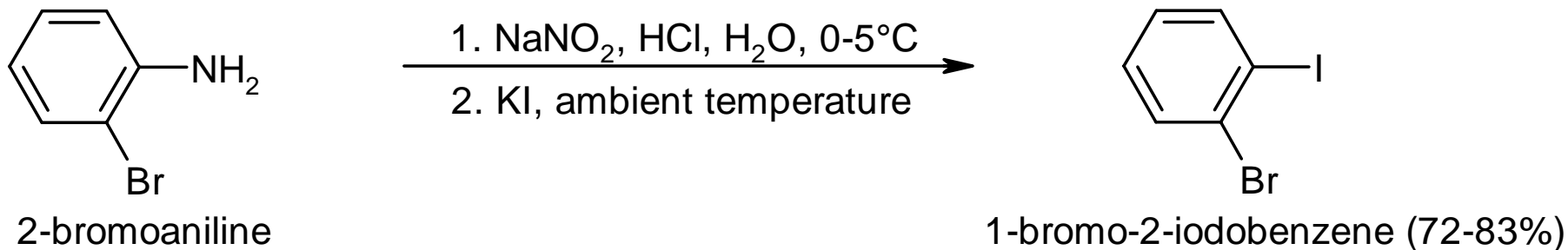
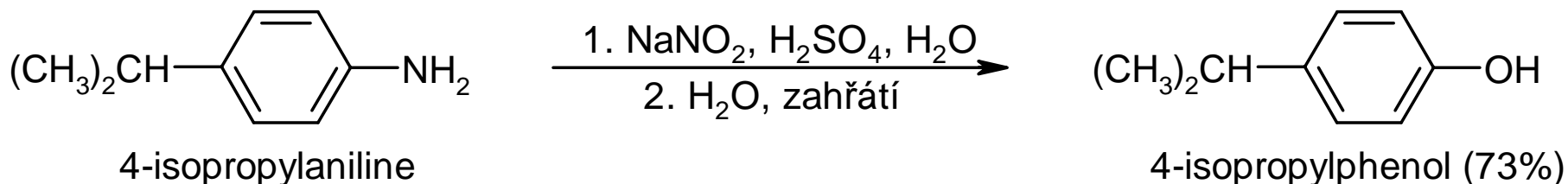
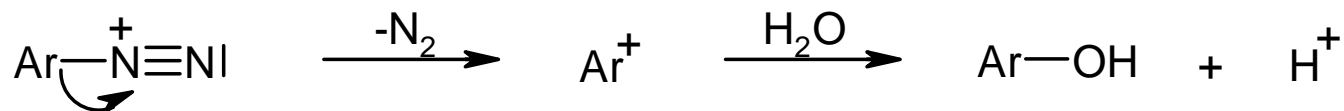




Organic Chemistry – chemistry of aromatics

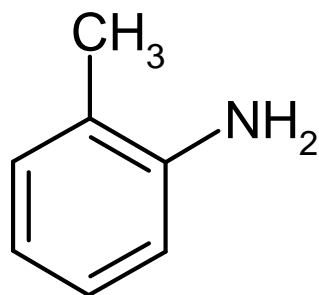


Amines – reactivity - diazonium salt synthetic utilisation – $S_{N(R)}$

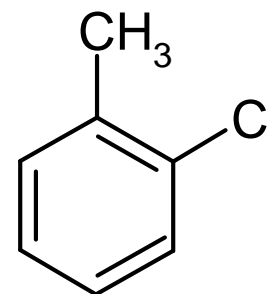
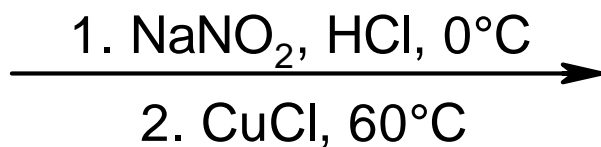




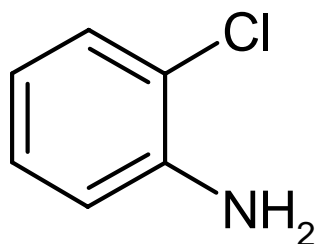
Amines – reactivity - diazonium salt synthetic utilisation – S_N(R)



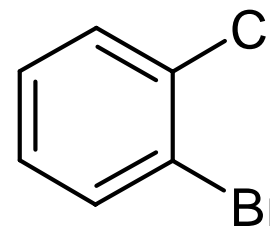
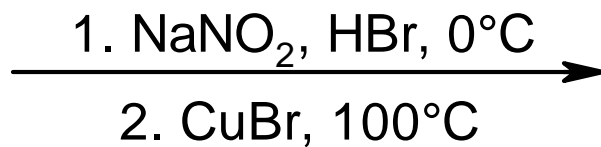
2-methylaniline



2-chlorotoluene (79%)



2-chloroaniline



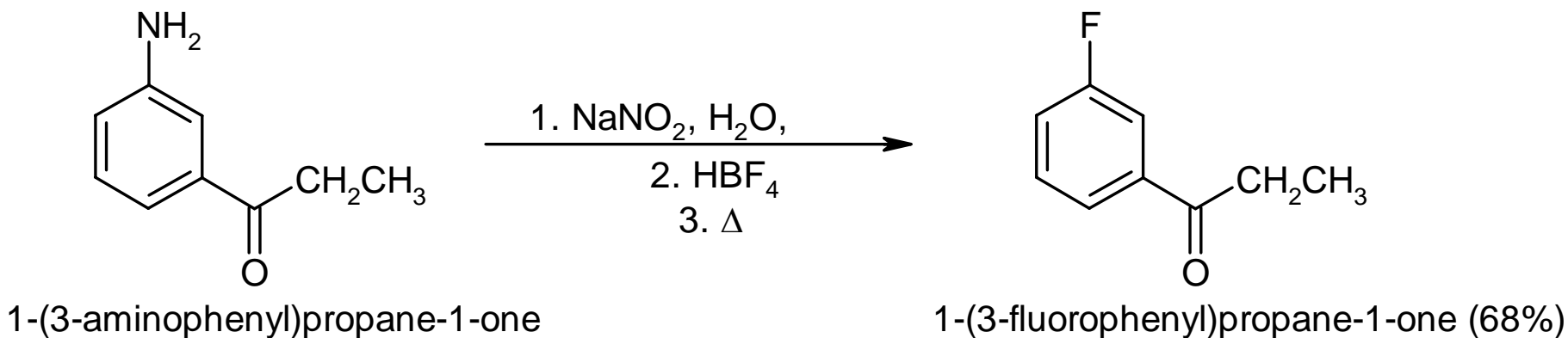
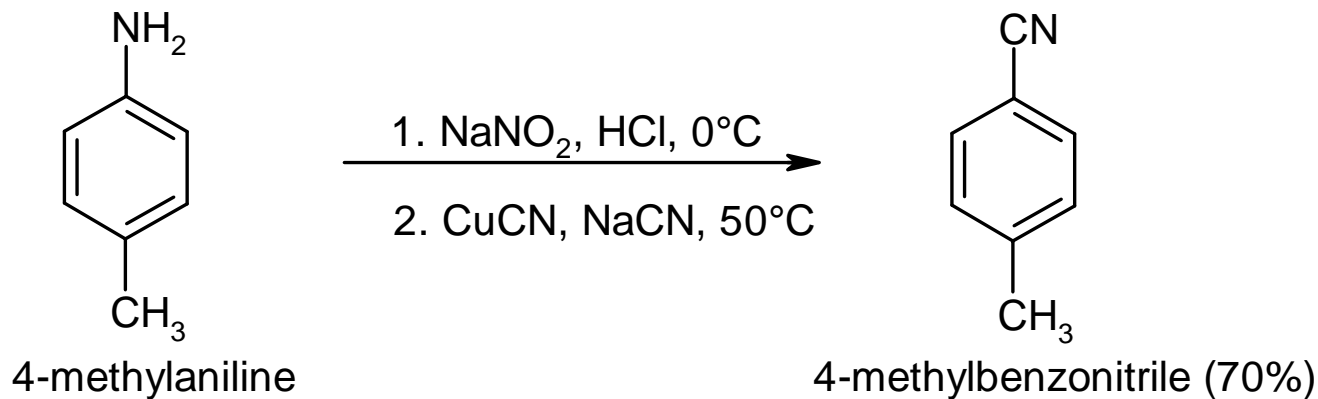
1-bromo-2-chlorobenzene (73%)



Organic Chemistry – chemistry of aromatics



Amines – reactivity - diazonium salt synthetic utilisation – $S_{N(R)}$

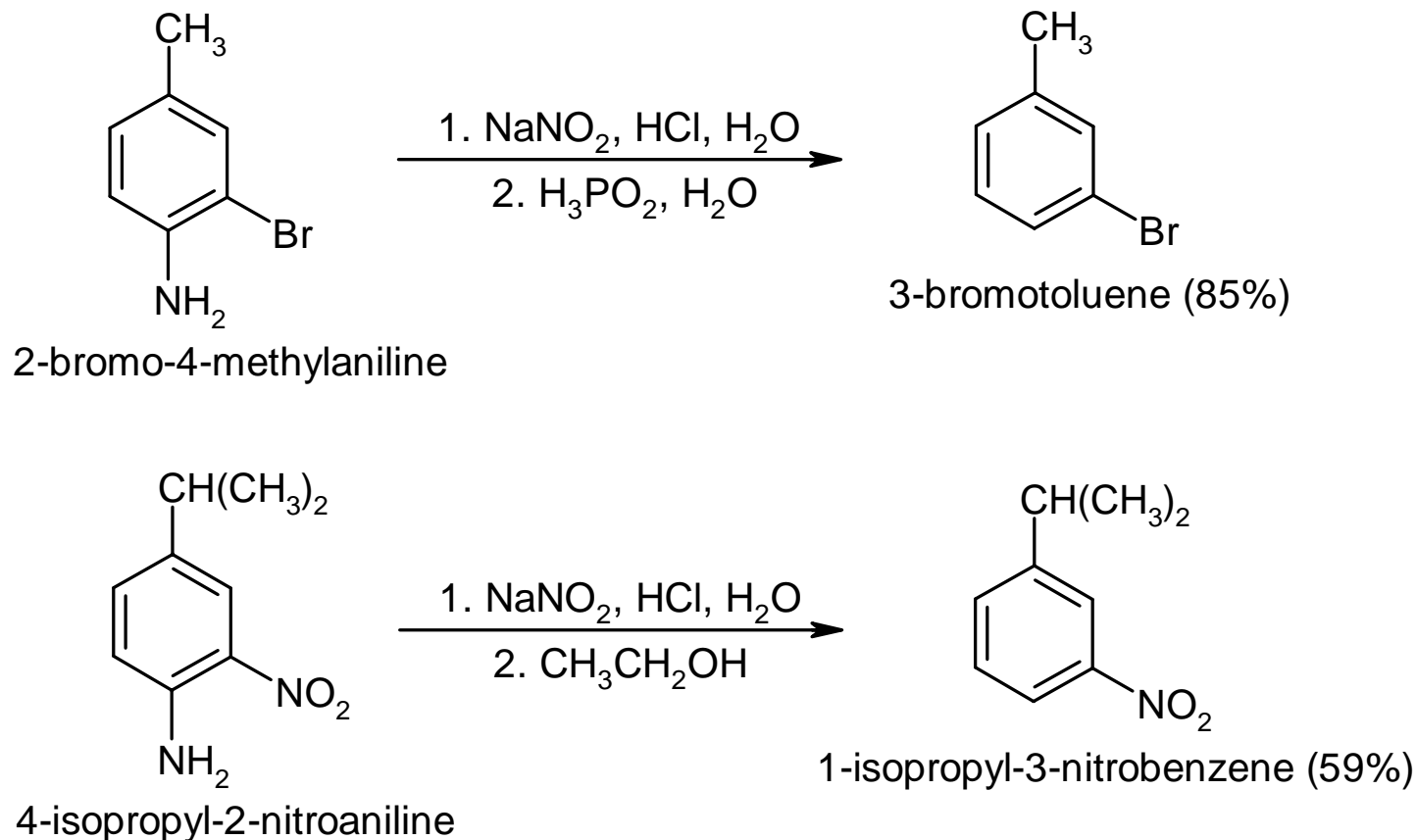
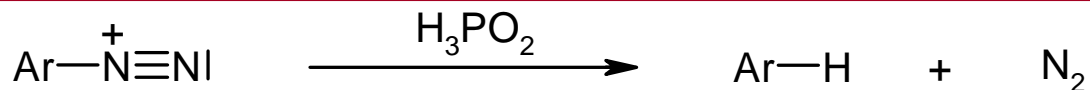




Organic Chemistry – chemistry of aromatics



Amines – reactivity - diazonium salt synthetic utilisation – $S_{N(R)}$

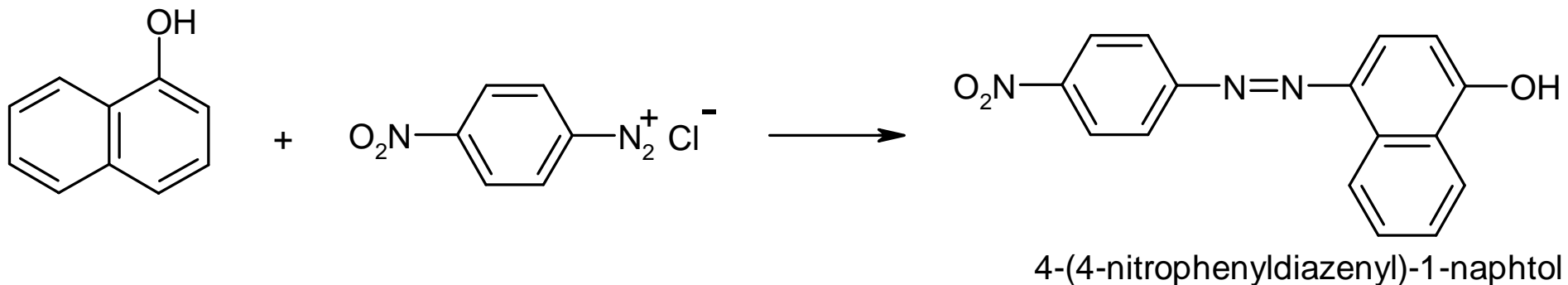
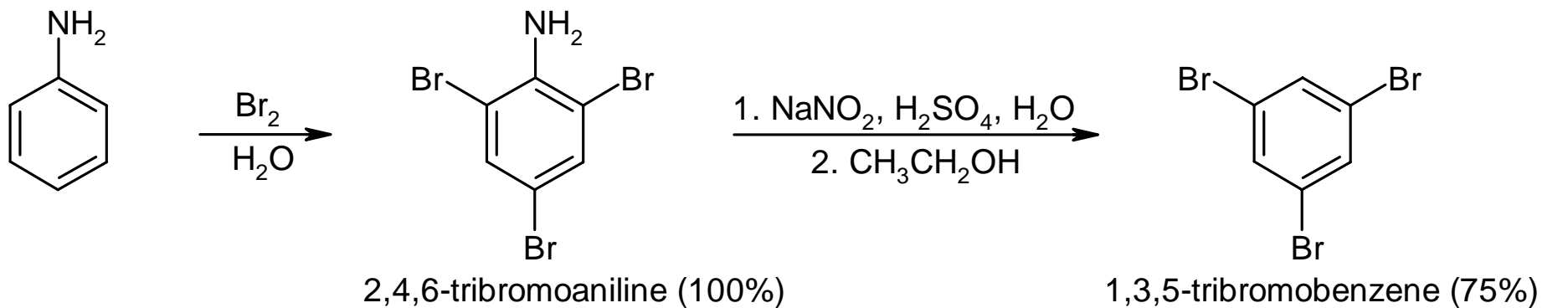




Organic Chemistry – chemistry of aromatics



Amines – reactivity - diazonium salt synthetic utilisation – $S_{N(R)}$





Organic Chemistry – chemistry of aromatics



Amines – reactivity - diazonium salt synthetic utilisation – $S_{N(R)}$

