




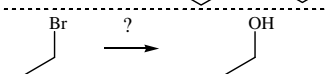
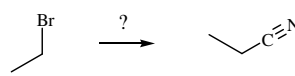
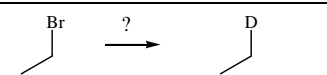
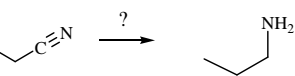
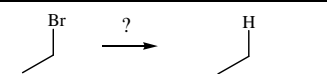
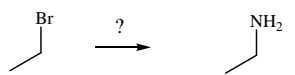
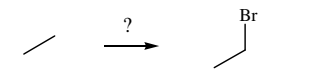
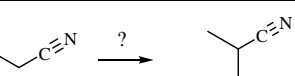

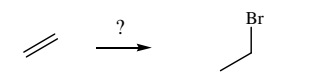
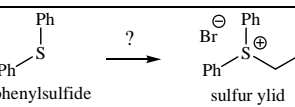

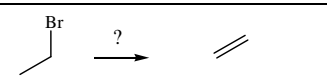
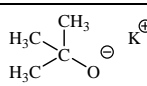
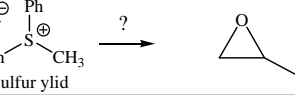

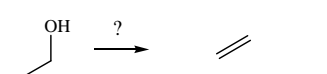
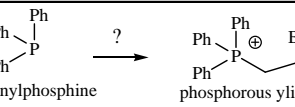

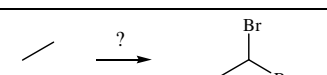
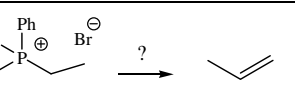


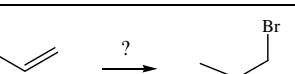
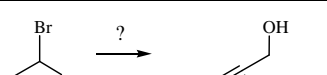

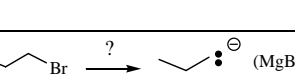
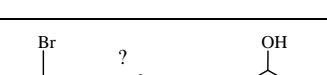

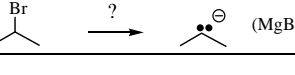

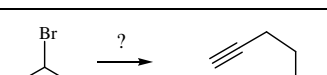

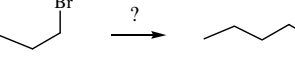

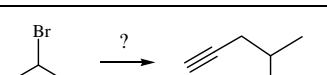

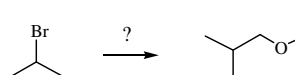

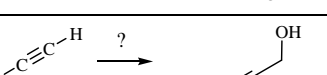

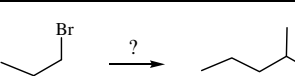

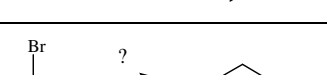
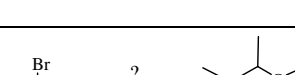

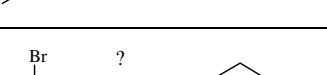


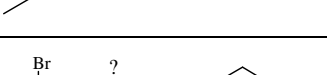
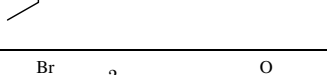




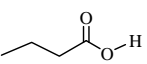
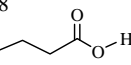
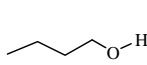

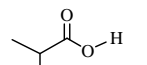
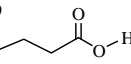
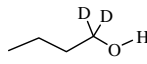

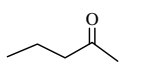
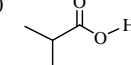
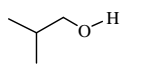

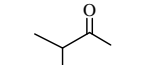
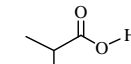
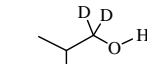

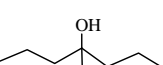

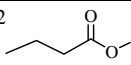
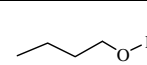

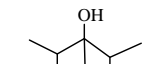

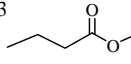
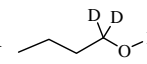

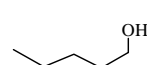

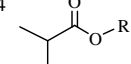
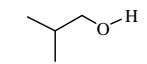

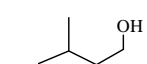

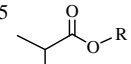
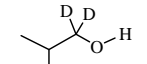

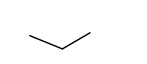


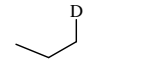


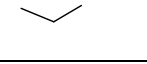



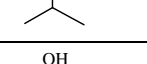



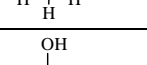



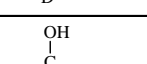

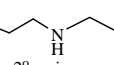
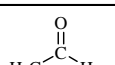
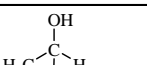
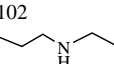
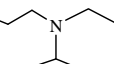
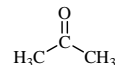
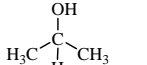


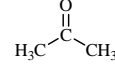
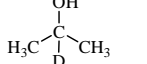

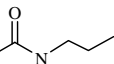




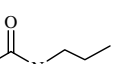





1C Chemistry. You should know the mechanism of every reaction below. (Ts = tosyl, Ph = phenyl)

1	CH_4 available = CO_2 , NaCN  	$\text{Br}_2 / \text{h}\nu$	20	$\text{H}_3\text{C}-\text{Br} \xrightarrow{?} \text{H}_3\text{C}-\text{C}(=\text{O})-\text{OH}$ carboxylic acids	1. Mg 2. $\text{O}=\text{C}=\text{O}$ 3. workup
2	$\text{H}_3\text{C}-\text{Br} \xrightarrow{?} \text{H}_3\text{C}-\text{O}-\text{H}$ alcohols	NaOH (ionic)	21	$\text{H}_3\text{C}-\text{C}(=\text{O})-\text{OH} \xrightarrow{?} \text{H}_3\text{C}-\text{C}(=\text{O})-\text{Cl}$ carboxylic acids → acid chlorides The 1C acid chloride is not stable, use an anhydride (beldw).	PCl_3
3	$\text{H}_3\text{C}-\text{Br} \xrightarrow{?} \text{H}_3\text{C}-\text{O}-\text{CH}_3$ ethers	$\text{CH}_3\text{OH} / \text{NaH}$ (ionic)	22	$\text{H}_3\text{C}-\text{NH}_2 \xrightarrow{?} \text{H}_3\text{C}-\text{N}(\text{CH}_3)_2$ 1° amines → 2° amines	1. pH=5, (-H ₂ O)  2. NaBH ₄
4	$\text{H}_3\text{C}-\text{Br} \xrightarrow{?} \text{H}_3\text{C}-\text{O}-\text{C}(=\text{O})-\text{H}$ esters	$\text{HO}-\text{C}(=\text{O})-\text{H}$ NaOH (ionic)	23	$\text{H}_3\text{C}-\text{N}(\text{CH}_3)_2 \xrightarrow{?} \text{H}_3\text{C}-\text{N}(\text{CH}_3)_3$ 2° amines → 3° amines	1. pH=5, (-H ₂ O)  2. NaBH ₄
5	$\text{H}_3\text{C}-\text{Br} \xrightarrow{?} \text{H}_3\text{C}-\text{S}-\text{H}$ thiols	NaSH (ionic)	24	$\text{H}_3\text{C}-\text{C}(=\text{O})-\text{Cl} \xrightarrow{?} \text{H}_3\text{C}-\text{C}(=\text{O})-\text{O}-\text{CH}_3$ acid chlorides → esters	$\text{H}_3\text{C}-\text{OH}$ alcohols
6	$\text{H}_3\text{C}-\text{Br} \xrightarrow{?} \text{H}_3\text{C}-\text{S}-\text{CH}_3$ thioethers sulfides	$\text{CH}_3\text{SH} / \text{NaOH}$ (ionic)	25	$\text{H}_3\text{C}-\text{C}(=\text{O})-\text{Cl} \xrightarrow{?} \text{H}_3\text{C}-\text{C}(=\text{O})-\text{S}-\text{CH}_3$ acid chlorides → thioesters	$\text{H}_3\text{C}-\text{SH}$ thiols
7	$\text{H}_3\text{C}-\text{Br} \xrightarrow{?} \text{H}_3\text{C}-\text{NH}_2$ 1° amines	1. NaN ₃ 2. LiAlH ₄ 3. workup	26	$\text{H}_3\text{C}-\text{C}(=\text{O})-\text{Cl} \xrightarrow{?} \text{H}_3\text{C}-\text{C}(=\text{O})-\text{NH}_2$ acid chlorides → 1° amides	NH_3 ammonia
8	$\text{H}_3\text{C}-\text{Br} \xrightarrow{?} \text{H}_3\text{C}-\text{C}\equiv\text{N}$ 2C nitriles	NaCN (ionic)	27	$\text{H}_3\text{C}-\text{C}(=\text{O})-\text{Cl} \xrightarrow{?} \text{H}_3\text{C}-\text{C}(=\text{O})-\text{N}(\text{H})-\text{CH}_3$ acid chlorides → 2° amides	$\text{H}_3\text{C}-\text{NH}_2$ 1° amines
9	$\text{H}_3\text{C}-\text{Br} \xrightarrow{?} \text{R}-\text{C}\equiv\text{C}-\text{CH}_3$ alkynes	$\text{R}-\text{C}\equiv\text{C}-\text{H}$ 1. NaNR ₂ 2. workup	28	$\text{H}_3\text{C}-\text{C}(=\text{O})-\text{Cl} \xrightarrow{?} \text{H}_3\text{C}-\text{C}(=\text{O})-\text{N}(\text{CH}_3)_2$ acid chlorides → 3° amides	$\text{H}_3\text{C}-\text{N}(\text{CH}_3)_2$ 2° amines
10	$\text{H}_3\text{C}-\text{Br} \xrightarrow{?} \text{H}_3\text{C}-\text{D}$ deuterated	LiAlD ₄ (ionic)	29	$\text{H}_3\text{C}-\text{C}(=\text{O})-\text{Cl} \xrightarrow{?} \text{H}_3\text{C}-\text{C}(=\text{O})-\text{O}-\text{C}(=\text{O})-\text{H}$ acid chlorides → anhydrides Use the 1C anhydride as an acid chloride	$\text{H}-\text{C}(=\text{O})-\text{OH}$ carboxylic acids
11	$\text{H}_3\text{C}-\text{Br} \xrightarrow{?} \text{Br}^{\ominus} \text{S}^{\oplus}(\text{Ph})_2 \text{CH}_3$ sulfur ylid	$\text{Ph}-\text{S}-\text{Ph}$ diphenylsulfide	30	$\text{H}_3\text{C}-\text{O}-\text{H} \xrightarrow{?} \text{H}_3\text{C}-\text{O}-\text{Br}$ bromoalkanes	HBr or PBr ₃
12	$\text{Br}^{\ominus} \text{S}^{\oplus}(\text{Ph})_2 \text{CH}_3 \xrightarrow{?} \text{epoxides}$	1. nBuLi 2. $\text{H}-\text{C}(=\text{O})-\text{H}$	31	$\text{H}_3\text{C}-\text{O}-\text{H} \xrightarrow{?} \text{H}_3\text{C}-\text{O}-\text{Ts}$ tosylates	TsCl / pyridine (tosylates)
13	$\text{H}_3\text{C}-\text{Br} \xrightarrow{?} \text{Ph}_3\text{P}^{\oplus} \text{CH}_3 \text{Br}^{\ominus}$ phosphorous ylid	Ph_3P triphenylphosphine	32	$\text{H}_3\text{C}-\text{O}-\text{Ts} \xrightarrow{?} \text{H}_3\text{C}-\text{O}-\text{Br}$ use 31 + 32 when rearrangement is a problem	NaBr (ionic)
14	$\text{Ph}_3\text{P}^{\oplus} \text{CH}_3 \text{Br}^{\ominus} \xrightarrow{?} \text{alkenes}$	1. nBuLi 2. $\text{H}-\text{C}(=\text{O})-\text{H}$	33	$\text{H}_3\text{C}-\text{O}-\text{H} \xrightarrow{?} \text{H}-\text{C}(=\text{O})-\text{H}$ aldehydes	CrO ₃ / pyridine (PCC)
15	$\text{H}_3\text{C}-\text{Br} \xrightarrow{?} \text{H}_3\text{C}\cdot (\text{MgBr})^{\oplus}$ Grignard reagent	Mg (Grignard)	34	$\text{H}_3\text{C}-\text{O}-\text{H} \xrightarrow{?} \text{H}-\text{C}(=\text{O})-\text{O}-\text{H}$ carboxylic acids	CrO ₃ / H ₂ O (Jones)
16	$\text{H}_3\text{C}-\text{Br} \xrightarrow{?} \text{H}_3\text{C}-\text{OH}$ 2C	1. Mg 2. $\text{H}-\text{C}(=\text{O})-\text{H}$ 3. workup	35	$\text{H}_3\text{C}-\text{O}-\text{H} \xrightarrow{?} \text{R}-\text{C}(=\text{O})-\text{O}-\text{CH}_3$ ester	$\text{R}-\text{C}(=\text{O})-\text{Cl}$
17	$\text{H}_3\text{C}-\text{Br} \xrightarrow{?} \text{H}_3\text{C}-\text{CH}_2-\text{OH}$ 3C	1. Mg 2.  3. workup	36	$\text{H}_3\text{C}-\text{OH} \xrightarrow{?} \text{H}_3\text{C}-\text{O}-\text{Br}$	HBr or PBr ₃ or 1. TsCl/pyridine 2. NaBr
18	$\text{H}_3\text{C}-\text{Br} \xrightarrow{?} \text{H}_3\text{C}-\text{CH}(\text{OH})-\text{CH}_3$ 3C	1. Mg 2. $\text{H}-\text{C}(=\text{O})-\text{O}-\text{R}$ 3. workup			
19	$\text{H}_3\text{C}-\text{Br} \xrightarrow{?} \text{H}_3\text{C}-\text{C}(=\text{O})-\text{CH}_3$ 3C	1. Mg 2. $\text{H}_3\text{C}-\text{C}\equiv\text{N}$ 3. workup			

36		NaOH (ionic)	54		NaCN (ionic)
37		LiAlD ₄ or NaBD ₄	55		1. LiAlH ₄ 3. workup
38		LiAlH ₄ or NaBH ₄	56		1. NaN ₃ 2. LiAlH ₄ 3. workup
39		Br ₂ hv	57		(enolate) 1. LDA 2.  3. workup
40		HBr, hv ROOR (cat.)	58		
41			59		1. nBuLi 2. 
42		H ₂ SO ₄ Δ (-H ₂ O)	60		
43		2 eqs. Br ₂ hv	61		1. nBuLi 2. 
44		1. 3 eqs. NaNR ₂ 2. workup	62		HBr, hv ROOR (cat.)
45		1. 3 eqs. NaNR ₂ 2.  3. workup	63		Mg (Grignard reagents) good carbanion nucleophiles
46		1. 3 eqs. NaNR ₂ 2.  3. workup	64		1. Mg 2.  3. workup
47		1. 3 eqs. NaNR ₂ 2.  3. workup	65		1. Mg 2.  3. workup
48		1. 3 eqs. NaNR ₂ 2.  3. workup	66		1. Mg 2.  3. workup
49		1. 1 eq. NaNR ₂ 2.  3. workup	67		1. Mg 2.  3. workup
50		ROH / NaH (ionic)	68		1. Mg 2.  3. workup
51		NaSH (ionic)	69		1. Mg 2.  3. workup
52		RSH / NaOH (ionic)			
53		NaOH (ionic) 			

<p>available = CO₂, NaCN  </p> <p>70  $\xrightarrow{?}$ </p>	<p>1. Mg 2. $\text{O}=\text{C}=\text{O}$ 3. workup</p>	<p>88  $\xrightarrow{?}$ </p>	<p>1. LiAlH₄ 2. workup</p>
<p>71  $\xrightarrow{?}$ </p>	<p>1. Mg 2. $\text{O}=\text{C}=\text{O}$ 3. workup</p>	<p>89  $\xrightarrow{?}$ </p>	<p>1. LiAlD₄ 2. workup</p>
<p>72  $\xrightarrow{?}$ </p>	<p>1. Mg 2. $\text{H}_3\text{C}-\text{C}\equiv\text{N}$ 3. workup</p>	<p>90  $\xrightarrow{?}$ </p>	<p>1. LiAlH₄ 2. workup</p>
<p>73  $\xrightarrow{?}$ </p>	<p>1. Mg 2. $\text{H}_3\text{C}-\text{C}\equiv\text{N}$ 3. workup</p>	<p>91  $\xrightarrow{?}$ </p>	<p>1. LiAlD₄ 2. workup</p>
<p>74  $\xrightarrow{?}$ </p>	<p>1. Mg 2.  3. workup</p>	<p>92  $\xrightarrow{?}$ </p>	<p>1. LiAlH₄ 2. workup</p>
<p>75  $\xrightarrow{?}$ </p>	<p>1. Mg 2.  3. workup</p>	<p>93  $\xrightarrow{?}$ </p>	<p>1. LiAlD₄ 2. workup</p>
<p>76  $\xrightarrow{?}$ </p>	<p>1. Mg 2.  3. workup</p>	<p>94  $\xrightarrow{?}$ </p>	<p>1. LiAlH₄ 2. workup</p>
<p>77  $\xrightarrow{?}$ </p>	<p>1. Mg 2.  3. workup</p>	<p>95  $\xrightarrow{?}$ </p>	<p>1. LiAlD₄ 2. workup</p>
<p>LiAlH₄ reactions (LAH), also LiAlD₄, often requires a workup step</p> <p>79  $\xrightarrow{?}$ </p>	<p>1. LiAlH₄ 2. workup</p>	<p>96 $\text{H}_3\text{C}-\text{C}\equiv\text{N}$ $\xrightarrow{?}$ </p>	<p>1. LiAlH₄ 2. workup</p>
<p>78  $\xrightarrow{?}$ </p>	<p>1. LiAlD₄ 2. workup</p>	<p>97 $\text{H}_3\text{C}-\text{C}\equiv\text{N}$ $\xrightarrow{?}$ </p>	<p>1. LiAlD₄ 2. workup</p>
<p>80  $\xrightarrow{?}$ </p>	<p>1. LiAlH₄ 2. workup</p>	<p>98  $\xrightarrow{?}$ </p>	<p>1. LiAlH₄ 2. workup</p>
<p>81  $\xrightarrow{?}$ </p>	<p>1. LiAlD₄ 2. workup</p>	<p>99  $\xrightarrow{?}$ </p>	<p>1. LiAlD₄ 2. workup</p>
<p>82  $\xrightarrow{?}$ </p>	<p>1. LiAlH₄ 2. workup</p>	<p>100  $\xrightarrow{?}$ </p>	<p>1. NaN₃ (ionic) 2. LiAlH₄ (ionic) 2. workup</p>
<p>83  $\xrightarrow{?}$ </p>	<p>1. LiAlD₄ 2. workup</p>	<p>101  $\xrightarrow{?}$ </p> <p>1° amines 2° amines</p>	<p>1. pH = 5 (-H₂O) 2. NaBH₄ (ionic)</p>
<p>84  $\xrightarrow{?}$ </p>	<p>1. LiAlH₄ 2. workup</p>	<p>102  $\xrightarrow{?}$ </p> <p>2° amines 3° amines</p>	<p>1. pH = 5 (-H₂O) 2. NaBH₄ (ionic)</p>
<p>85  $\xrightarrow{?}$ </p>	<p>1. LiAlD₄ 2. workup</p>	<p>103  $\xrightarrow{?}$ </p> <p>1° amides</p>	<p>NH₃ ammonia</p>
<p>86  $\xrightarrow{?}$ </p>	<p>1. LiAlH₄ 2. workup</p>	<p>104  $\xrightarrow{?}$ </p> <p>2° amides</p>	<p> 1° amines</p>
<p>87  $\xrightarrow{?}$ </p>	<p>1. LiAlD₄ 2. workup</p>	<p>105  $\xrightarrow{?}$ </p> <p>3° amides</p>	<p> 2° amines</p>
		<p>106 I tried to get most of our reactions in this list. There are probably some that I missed, so if you think of any, please let me know.</p>	

Write out some of your own reaction equations.

available = CO ₂ , NaCN  			
36	?		54
	→		→
37	?		54
	→		→
38	?		54
	→		→
39	?		54
	→		→
40	?		54
	→		→
40	?	⊕	54
	→		→
40	?		54
	→		→
40	?		60
	→		→
40	?		60
	→		→
40	?		60
	→		→
40	?		60
	→		→
40	?		60
	→		→
40	?		60
	→		→
40	?		60
	→		→
50	?		60
	→		→
50	?		60
	→		→
50	?		60
	→		→
50	?		70
	→		→

Mechanisms to know in textbook.

Chapter 9

SN2 and E2 – Chapter 9, pages 250-
 Acyl substitution – base hydrolysis of an ester, Chapter 9, page 262
 Double E2 to make alkynes – Chapter 9, pages 271-2
 SN1 and E1 – Chapter 9, pages 274-5
 Rearrangements – Chapter 9, pages 279-82, problem 25, page 287
 ROH \rightarrow RBr using HBr and PBr₃ – Chapter 9, pages 285-286
 ROH \rightarrow ROTs \rightarrow RBr (tosylates) – Chapter 9, pages 288-289
 ROH \rightarrow alkenes (E1 reactions, -H₂O) – Chapter 9, pages 290
 Problem 30 has mechanism of each type – Chapter 9, page 294
 Templates for SN/E reactions – Chapter 9, page 295
 Worked out problems, all types – Chapter 9, pages 296-297

Chapter 10

Free radical substitution of C-H \rightarrow C-Br, Chapter 10, page 301
 Free radical addition to an alkene of H-Br, Chapter 10, page 320

Chapter 11

Oxidation of ROH using CrO₃/pyridine and CrO₃/H₂O \rightarrow aldehydes, ketones, carboxylic acids
 Chapter 11, pages 328-331 (PCC and Jones oxidations)
 LiAlH₄ reductions of aldehydes, ketones, esters, carboxylic acids, nitriles, imines – Chapter 11,
 pages 333-337
 Imine synthesis from amines + carbonyls (alds and ketones) – Chapter 11, pages 336-337
 Making acid chlorides from carboxylic acids, Chapter 11, page 338
 Reactions of acid chlorides (acyl substitution), Chapter 11 page 339
 Relative reactivity of C=O functional groups, Chapter 11, pages 340-44
 Various possible synthetic transformations (no mechanisms), Chapter 11, pages 344-56

Chapter 12

Sulfur ylid synthesis and reactions to make epoxides using aldehydes and ketones, Chapter 12,
 pages 359-361
 Grignard reagents and reactions, Chapter 12, pages 361-368 (aldehydes, ketones, carbon dioxide,
 esters, nitriles, epoxides)
 Cuprate reactions (that do not work with Grignards), Chapter 12, pages 369-373
 Strong base/nucleophile with aldehydes and ketones, Chapter 12, pages 376-8
 Strong base/nucleophile with epoxides, Chapter 12, pages 379-380
 Making enolates and their reactions, Chapter 12, pages 380-2
 Synthesis strategies, C₄ and C₅ target molecules, Chapter 12, pages 397-403
 Wittig reaction, phosphorus ylids + aldehyde or ketone \rightarrow alkenes (E or Z), Chapter 12, pages 387-90