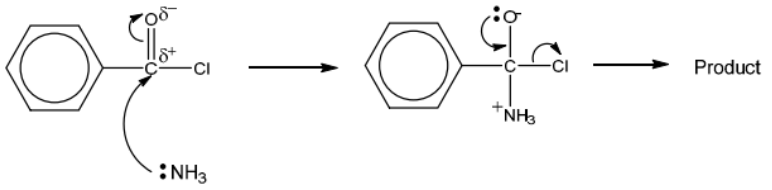
33. Carboxylic acids and derivatives

33.3 Acyl chlorides

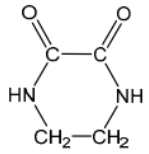
Paper 4

Marking Scheme

Q1.

(d)	 **M1 / M2** *any two for one mark, all four for two marks:* • lone pair on N • correct arrow from lone pair N to C (of C=O) • correct dipole on C=O • correct arrow from the C=O bond to O atom **M3** correct intermediate **M4** arrow from O(−) to C–O bond **AND** arrow from C–Cl bond to Cl **ALLOW** arrow from anywhere on O⁻ to C–O bond	**4**

Q2.

(b)(i)	$(COOH)_2 + 2SOCl_2 \rightarrow (COCl)_2 + 2HCl + 2SO_2$	**1**
(b)(ii)	CO_2 [1]  [1]	**2**

Q3.

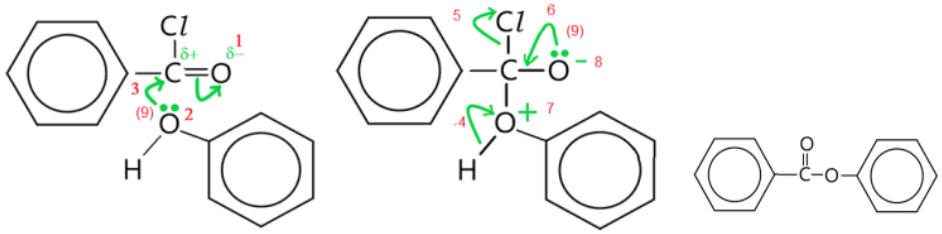
(a)(i)	ClOCCOCl	[1]	**1**
(a)(ii)	PCl_3 / PCl_5	[1]	**1**

Q4.

(d)(i)	$CH_3COOH + SOBr_2 \rightarrow CH_3COBr + HBr + SO_2$	1

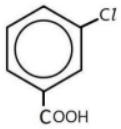
(d)(ii)	**M1** acyl bromides (easiest) > acyl chlorides > alkyl chlorides (hardest) **M2 M3** *Any two from:* *Acyl bromides easiest* • in acyl bromides C–Br is much weaker **ORA AND** due to less orbital overlap / Br having a larger atomic radii *Acyl halides easier than alkyl chlorides* • carbon in C–Cl / C–Br / C–X bond is more δ+/electron deficient **OR** C–Cl / C–Br bond is weaker (than C-Cl in alkyl chlorides) **AND** attached to an oxygen atom / two electronegative atoms / electron withdrawing C=O group **ORA** *alkyl chlorides hardest* • in alkyl chlorides C–Cl bond strengthened **AND** by positive inductive effect / electron donating effect of alkyl / R group	3

Q5.

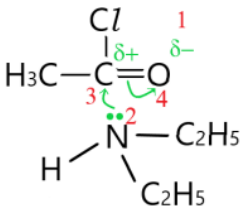
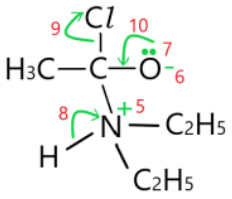
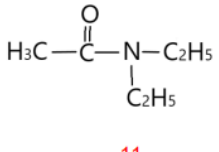
(b)(i)	 and HCl [10] The red numbers refer to points 1 to 10 in the verbal MS that follows.	
	box one: • 1 dipole on C=O • 2 curly arrow from O of phenol to C of acyl chloride • 3 curly arrow from bond of C=O to O of acyl chloride box two: • 4 curly arrow from O-H bond to what was O of phenol • 5 curly arrow from C-Cl bond to what was Cl of acyl chloride • 6 curly arrow from O to reform C=O • 7 + charge on what was O of phenol • 8 – charge on what was O of acyl chloride • 9 curly arrow start close to LP for bullet 3 OR 6 (from LP on O) box three: • 10 HCl / H^+Cl^- any two [1] any five [2] any eight [3] all ten [4]	4
(b)(ii)	(nucleophilic) addition-elimination [1]	1

(c)	chlorobenzene, chloroethane, benzoyl chloride [1] u / c explanation linked to their order • correct link to: strengthening (ArC*l* / RC*l*) C-C*l* bond OR weakening (RCOC*l*) C-C*l* bond OR C-C*l* bond has partially double bond character (ArC*l*) OR C-C*l* is more difficult to break (linked correctly) chlorobenzene: • lone pair / p-orbital on C*l* overlaps / delocalised / incorporated with ring benzoyl chloride: • C of C-C*l* has most electron deficient OR has an electronegative oxygen atom / two electronegative atoms / electron withdrawing C=O group chloroethane • electron donating effect / positive inductive effect of alkyl / R group any two [1] any three [2]	**3**

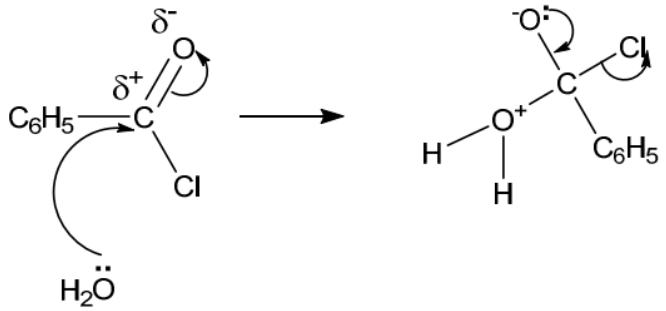
Q6.

(c)(ii)	 L [1]  M [1] PCl_3 + heat **OR** $SOCl_2$ **OR** PCl_5 [1]	**3**

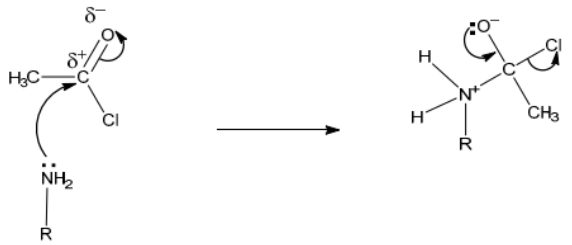
Q7.

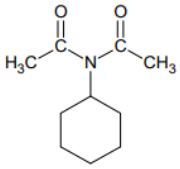
(d)(i)	box one  box two  box three  box one: 1 dipole on C=O 2 LP on N of amine [1] 3 CA from N of amine to C of acyl chloride 4 CA from = to O of acyl chloride [1] box two: 5 + on what was N of amine and nowhere else 6 – on what was O of acyl chloride and nowhere else 7 LP on what was O of acyl chloride [1] 8 CA from N-H bond to what was N of amine 9 CA from C-C*l* bond to what was C*l* of acyl chloride 10 CA from (LP on) O to reform C=O [1] box three: 11 HC*l*	**4**
(d)(ii)	Addition-elimination	**1**

Q8.

(c)(i)	$POCl_3$ and HC*l* **AND** SO_2 and HC*l*	**1**
(c)(ii)	all the by-products / SO_2 and HC*l* are gaseous **OR** no liquid by-products formed	**1**
(d)(i)	 On the left-hand side: • lone pair on O • correct arrow from O to C (of C=O) • dipole on C=O • correct arrow on C=O **M1** / **M2** Two correct for one mark, four correct for two marks On the right-hand side: **M3** correct intermediate **M4** arrow from lone pair on O^- to C-O bond **AND** arrow from C-C*l* to C*l*	**4**
(d)(ii)	addition-elimination	**1**

Q9.

(b)(i)	(nucleophilic) addition-elimination	1
(b)(ii)	 **M1 / M2** • lone pair on N • correct arrow from (lone pair) N to C (of C=O) • dipole on C=O • correct arrow on C=O two for one mark, four for two marks **M3** correct intermediate **M4** arrow from lone pair on O^- to C-O bond **AND** arrow from C-C*l* to C*l*	4

(b)(iii)		1

Q10.

(c)(i)	conc. HNO_3 and H_2SO_4 (25 °C < T ⩽ 60 °C) [1] Sn and conc. HC*l* and reflux (followed by NaOH(aq)) [1]	2

Q11.

(b)	D ethanoyl chloride [1] E correct phenyl ester [1] F correct amide [1]	3

Q12.

(a)	**M1:** acyl chlorides > alkyl chlorides > aryl chlorides fastest slowest **M2 / 3:** *Any two from:* • *acyl chlorides* carbon in C-C*l* bond is more electron deficient since it is also attached to an oxygen atom **OR** C-C*l* bond is weakest / weakened in acyl chlorides since it is also attached to an oxygen atom / two electronegative atoms • *aryl chlorides* (no hydrolysis) C-C*l* bond is part of delocalised system / partially double bond character (so C-C*l* bond is stronger) **OR** lone pair / p-orbital on C*l* delocalises with π ring (so C-C*l* bond is stronger) • *alkyl chlorides* C-C*l* bond strengthened by electron donating effect / positive inductive effect of alkyl / R group (as compared to acyl chlorides) **OR** carbon atom has a smaller δ+ and the C-C*l* bond is stronger (than the C-C*l* bond in COC*l*) due to (the carbon) being only attached to one electronegative atom	**3**

Q13.

(a)	PCl_5 **OR** PCl_3 **OR** $SOCl_2$ [1]	**1**
(b)(i)	amide [1]	**1**
(b)(ii)	HC*l* / hydrogen chloride **OR** $C_2H_5NH_3Cl$ / ethylammonium chloride [1]	**1**

Q14.

(c)	condensation/ addition-elimination	**1**

Q15.

(c)(i)	CH_3COCl [1] ethanoyl chloride [1]	**2**
(c)(ii)	Step 1: PCl_5 / PCl_3 / $SOCl_2$ or names [1] Step 2: NH_3 / ammonia [1]	**2**

Q16.

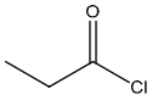
(f)(i)	$CH_3COCl + CH_3NH_2 \rightarrow CH_3CONHCH_3 + HCl$ **M1** Correct formulae of CH_3COCl **or** $CH_3CONHCH_3$ **M2** rest of the equation	**2**
(f)(ii)	condensation or addition-elimination	**1**

Q17.

(b)(i)	correct acid chloride	**1**
(b)(ii)	NH_3 or ammonia	**1**

(c)	**M1:** $(C_5NH_4)COOH$ or $(C_5NH_5)^+COOH$ **M2:** $(C_5NH_4)COO^-(Na^+)$ or $(C_5NH_4)COONa$	**2**

Q18.

(d)	PCl_5 or PCl_3 (+heat) or $SOCl_2$ (added to propanoic acid)	**1**
	product of first step: 	**1**
	add product of first step to phenol in NaOH	**1**