Daignault, R. A.; Eliel, E. L. Org. Synth., Coll. Vol. V 1973, 303.

A: Activation of the carbonyl group by protonation. B: Addition of ethylene glycol to the activated carbonyl group. C: Proton transfer. D: Elimination of water helped by the oxygen lone pair. E: Intramolecular addition of the second hydroxy group.

Baker, R.; Cooke, N. G.; Humphrey, G. R.; Wright, S. H. B.; Hirshfield, J. J. Chem. Soc., Chem. Commun. 1987, 1102.

A: Activation of the carbonyl group by protonation. **B**: Addition of MeOH to the activated carbonyl group. **C**: Proton transfer. **D**: Elimination of water helped by the oxygen lone pair. **E**: Addition of MeOH and deprotonation to form a dimethyl acetal. **F**: Trimethyl orthoformate serves as a scavenger of water to shift the equilibrium to the product side. Protonation followed by elimination of MeOH. **G**: Addition of water. **H**: Proton transfer. **I**: Elimination of MeOH followed by deprotonation to form HCO₂Me.

A010

Aben, R. W. M.; Hanneman, E. J. M.; Scheeren, J. M. Syn. Commun. 1980, 10, 821.

A: Protonation. B: Cleavage of the dioxolane ring helped by the oxygen lone pair. C: Deprotonation to form an enol ether. D: Bromination of the electron-rich enol ether. E: Intramolecular addition of the hydroxy group. Opening of the dioxolane ring of the product is more difficult because of the electron-withdrawing bromine atom.

Aon

Kendall, E. C.; McKenzie, B. F. Org. Synth., Coll. Vol. I 1941, 21.

Strecker amino acid synthesis. A: Protonation of the carbonyl group. B: Addition of NH₃ to the carbonyl group followed by deprotonation to form a hemiaminal. C: Protonation followed by elimination of water is helped by the nitrogen lone pair to form an iminium ion. D: Addition of a cyanide ion to form an aminonitrile. E: Acidic hydrolysis of the nitrile. The amino group is protonated throughout the reaction. F: Protonation of the nitrile to form a reactive nitrilium ion. G: Addition of water to the nitrilium ion. H: Deprotonation and tautomerization. I: Protonation of the resulting amide followed by addition of water. J: Proton transfer. K: Elimination of NH₃ followed by deprotonation to form the product.

A012

Campaigne, E.; Archer, W. L. Org. Synth., Coll. Vol. IV 1963, 331.

Vilsmeier reaction. A: The electron-rich oxygen of DMF attacks POCl₃ (oxygen of amides is generally more reactive toward electrophiles under neutral conditions). **B**: Addition of chloride ion followed by

elimination of a dichlorophosphate ion to form the Vilsmeier reagent. **C**: Addition of an electron-rich aromatic ring to Vilsmeier reagent followed by rearomatization. **D**: Elimination of chloride ion helped by the nitrogen lone pair leads to the formation of an iminium ion. **E**: Addition of water to the iminium ion. **F**: Proton transfer followed by elimination of Me₂NH.

Maxwell, C. E. Org. Synth., Coll. Vol. III 1955, 305.

Mannich reaction. **A**: Protonation of formaldehyde followed by addition of Me₂NH to the carbonyl group. **B**: Proton transfer followed by elimination of water to form an iminium ion. **C**: Tautomerization of the ketone to form an enol. **D**: Attack of the electron-rich enol to the iminium ion.

MeO
$$\stackrel{\leftarrow}{NH_2OH}$$
 $\stackrel{\leftarrow}{A}$ $\stackrel{\leftarrow}{Ar}$ $\stackrel{\leftarrow}{H}$ $\stackrel{\leftarrow}$