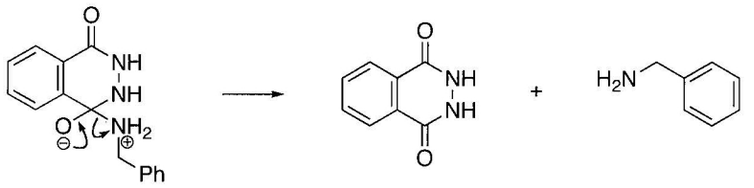
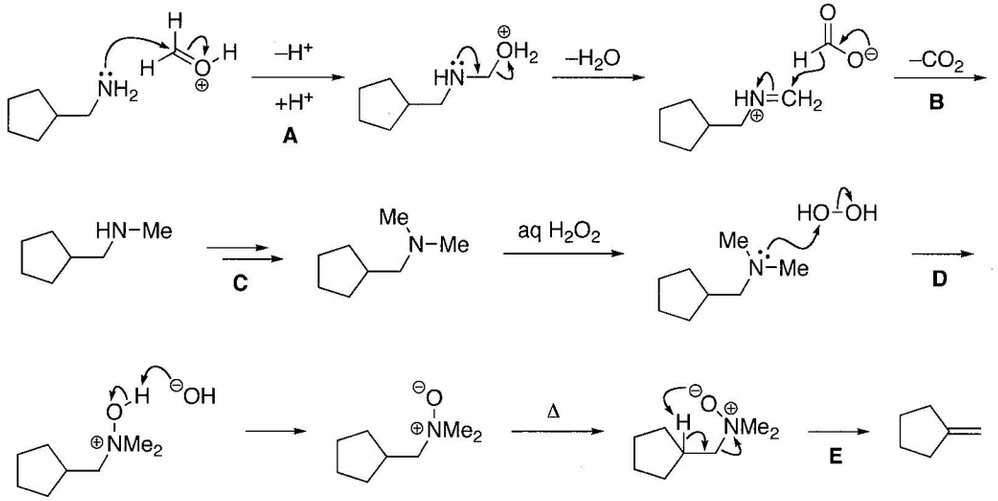


Manske, R. H. F. *Org. Synth., Coll. Vol. II* **1943**, 83.

Gabriel synthesis. **A**: pKa RCONHCOR = 9.6, HCO_3^- = 10.3. **B**: Alkylation. **C**: Addition of H_2NNH_2 to the imide to form a hydrazide. **D**: Intramolecular addition of the amino group of the hydrazide to the amide carbonyl to release benzylamine.

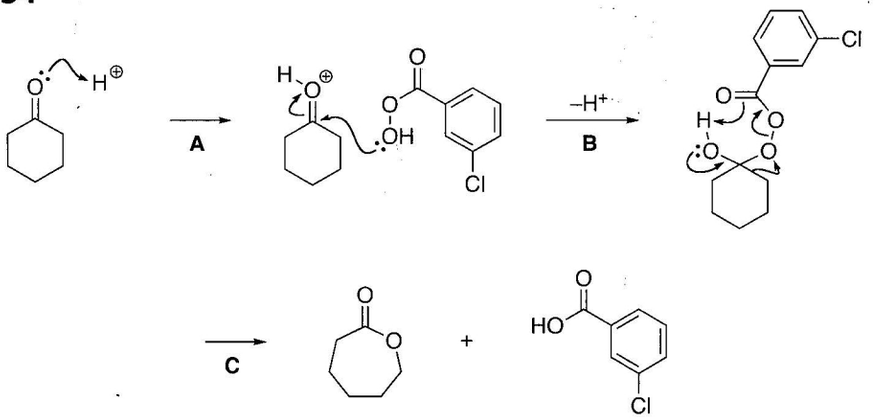
A053



Cope, A. C.; Bumgardner, C. L.; Schweizer, E. E. *J. Am. Chem. Soc.* **1957**, *79*, 4729.

Eschweiler-Clarke methylation (**A**-**C**) and Cope elimination (**E**). **A**: Addition of the amine to formaldehyde followed by dehydration to form an iminium ion. **B**: Hydride transfer from a formate anion to the iminium ion with generation of CO_2. **C**: Iteration of the same steps. **D**: Oxidation of the tertiary amine to form an *N*-oxide. **E**: *syn*-Elimination.

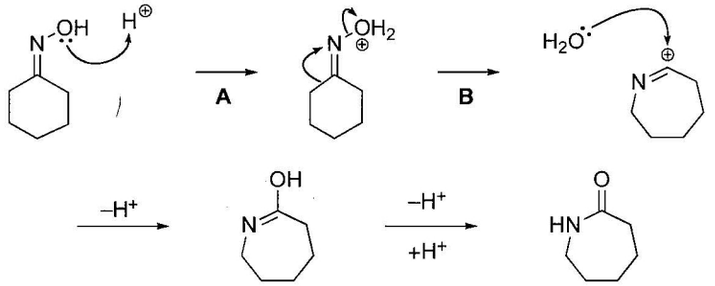
A054



Krow, G. R. *Org. React.* **1993**, *43*, 251.

Baeyer-Villiger oxidation. **A**: Activation of the carbonyl group by protonation. **B**: Addition of *m*CPBA to the carbonyl group. **C**: 1,2-Alkyl shift helped by the oxygen lone-pair with cleavage of the peroxide to form a lactone.

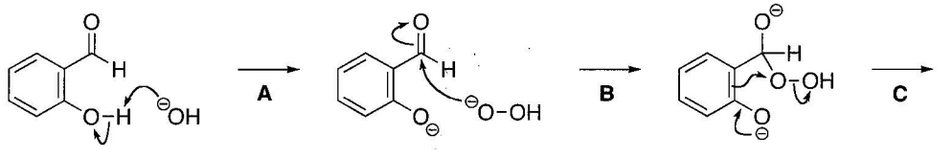
A055

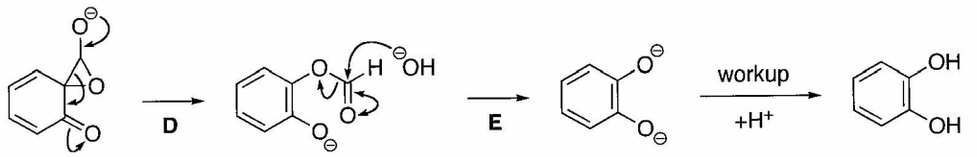


Eck, J. C.; Marvel, C. S. *Org. Synth., Coll. Vol. II* **1943**, 76.

Beckmann rearrangement. **A**: Protonation of the oxime. **B**: Migration of the alkyl substituent with simultaneous cleavage of the N-O bond.

A056

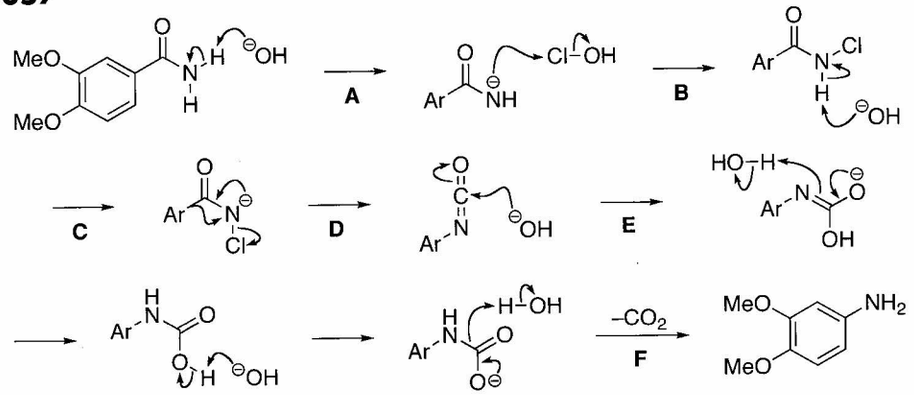




Dakin. H. D. *Org. Synth., Coll. Vol. I* **1941**, 149.

Dakin reaction. **A**: Deprotonation of the phenol (pKa PhOH = 10, H_2O = 15.7). **B**: Addition of hydroperoxide ion to the carbonyl group. **C**: Attack of the electron-rich aromatic ring to the peroxide oxygen with cleavage of the O-O bond to form an epoxide. **D**: Cleavage of the epoxide to restore the aromaticity. **E**: Hydrolysis of the resulting formate.

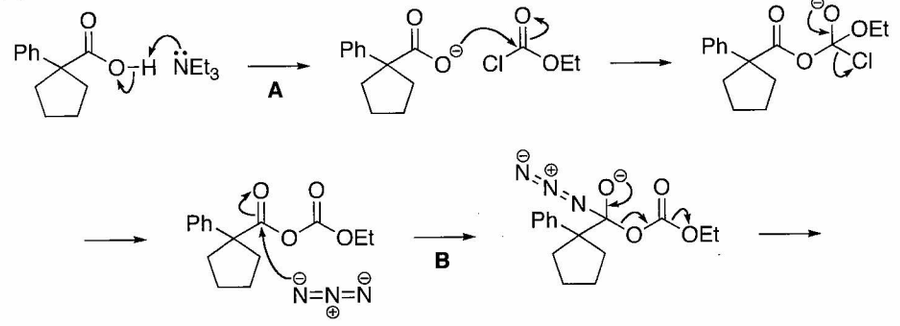
A057

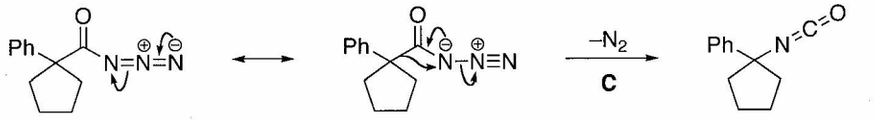


Buck. J. S.; Ide, W. S. *Org. Synth., Coll. Vol. II* **1943**, 44.

Hofmann rearrangement. **A**: pKa $RCONH_2$ = 17, H_2O = 15.7. **B**: Chlorination of the amide anion. **C**: Deprotonation. **D**: The anion on the nitrogen atom induces migration of the aromatic ring with cleavage of the N-Cl bond to form an isocyanate. **E**: Addition of hydroxide ion to the isocyanate. **F**: Decarboxylation.

A058

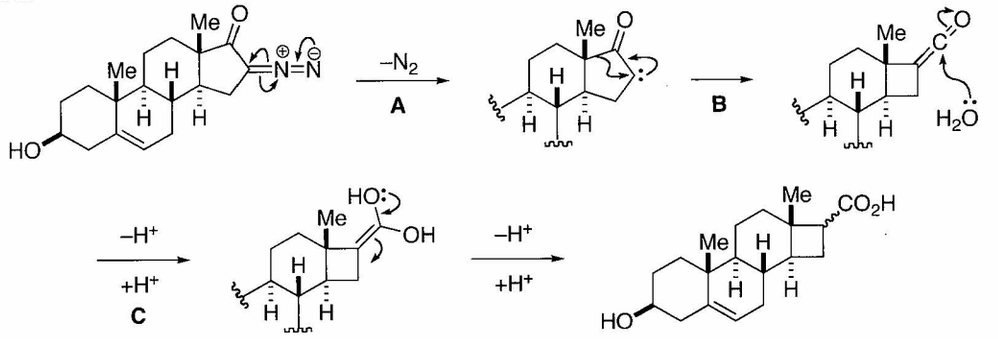




Kaiser, C.; Weinstock, J. *Org. Synth., Coll. Vol. VI* **1988**, 910.

Curtius rearrangement. **A**: Formation of a mixed anhydride. **B**: Addition of azide ion to the mixed anhydride occurs at the more electron-deficient carbonyl group to form an acyl azide. **C**: Migration of the carbon atom to the nitrogen proceeds with retention of configuration as N_2, an extremely good leaving group, departs from the molecule.

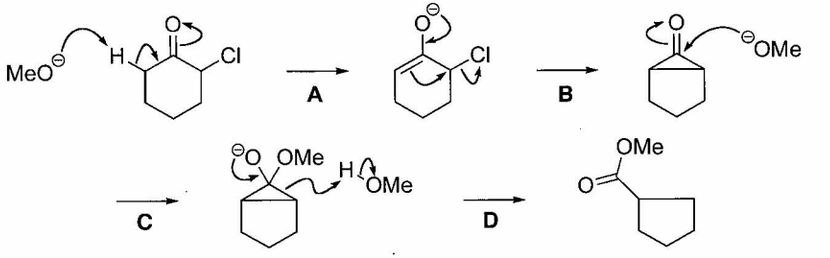
A059



Wheeler, T. N.; Meinwald, J. *Org. Synth., Coll. Vol. VI* **1988**, 840.

Wolff rearrangement. **A**: Photo-induced generation of a carbene. **B**: Insertion of the carbene to the C-C bond results in a ring contraction to form a ketene. **C**: Addition of water to the ketene.

A060



Goheen, D. W.; Vaughan, W. R. *Org. Synth., Coll. Vol. IV* **1963**, 594.

Favorskii rearrangement. **A**: Deprotonation to form an enolate. **B**: Formation of a cyclopropanone. **C**: Addition of methoxide ion to the carbonyl group. **D**: Cleavage of the cyclopropane ring with simultaneous protonation.