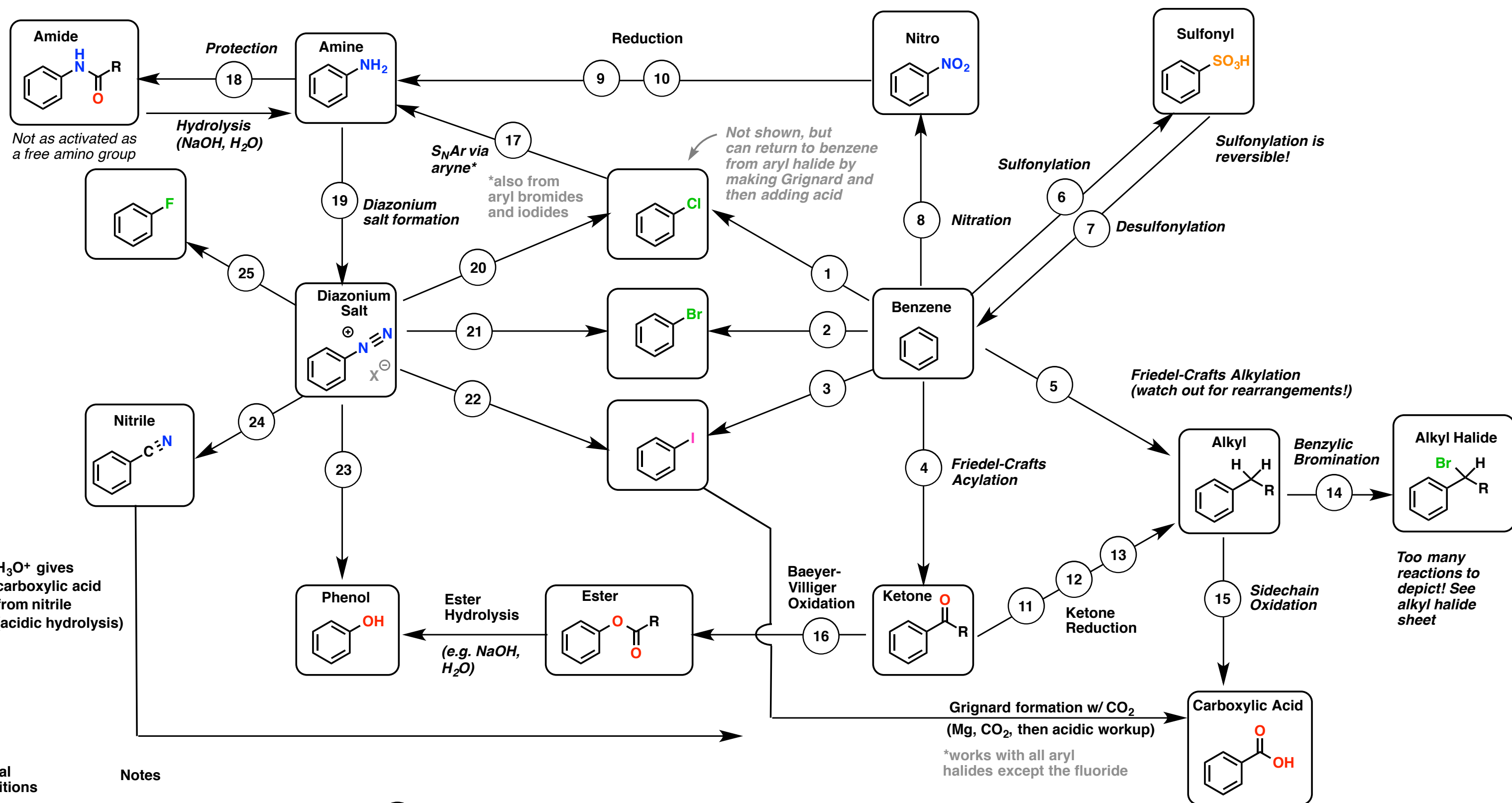


Reaction Map: Reactions of Benzene And Related Aromatic Compounds

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| Reaction | Name | Typical Conditions | Notes |
|----------|-----------------------------|--|---|
| 1 | Chlorination | Cl ₂ , FeCl ₃ | Catalytic in FeCl ₃ (can use other Lewis acids, like AlCl ₃ , ZrCl ₄ , etc.) |
| 2 | Bromination | Br ₂ , FeBr ₃ | Catalytic in FeBr ₃ |
| 3 | Iodination | I ₂ , oxidant | Stoichiometric oxidant required e.g. CuBr ₂ , HNO ₃ /H ₂ SO ₄ |
| 4 | Friedel-Crafts Acylation | $\text{R}-\text{C}(=\text{O})-\text{Cl}$, AlCl ₃ | No rearrangements occur Fails when <i>meta</i> -directing substituents present (too deactivating) |
| 5 | Friedel-Crafts Alkylation | $\text{R}-\text{Cl}$, AlCl ₃ | Rearrangements can occur with primary alkyl halides Can also use alkene + strong acid |
| 6 | Sulfonylation | SO ₃ , H ₂ SO ₄ | - |
| 7 | Desulfonylation | H ₂ SO ₄ , heat | Allows use of SO ₃ H as blocking group |
| 8 | Nitration | HNO ₃ , H ₂ SO ₄ | Makes NO ₂ ⁺ in solution, which is the key electrophile |
| 9 | Nitro group reduction | Zn, HCl | Reduction of nitro group with metal and acid; can also use Fe, Sn, or SnCl ₂ |
| 10 | Nitro group reduction | Pd-C, H ₂ (or Pt-C, or Ni) | Catalytic hydrogenation |
| 11 | Wolff-Kishner reduction | KOH, NH ₂ NH ₂ , HOCH ₂ CH ₂ OH, heat | Basic, requires high heat |
| 12 | Clemmensen reduction | Zn(Hg), H+ | Requires acidic conditions |
| 13 | Catalytic hydrogenation | Pd-C, H ₂ | Requires high pressures; only works for benzylic ketones |
| 14 | Benzylic bromination | Br ₂ , peroxides | Only attaches to benzylic position. |
| 15 | Sidechain oxidation | KMnO ₄ , acid | Benzylic carbon must have at least one C-H bond (can also use H ₂ CrO ₄) |
| 16 | Baeyer-Villiger oxidation | RCO ₃ H (e.g. <i>m</i> -CPBA) | RCO ₃ H is a peroxyacid |
| 17 | S _N Ar via aryne | NaNH ₂ , NH ₃ , -30°C | Elimination gives an aryne intermediate, which can be trapped with dienes (Diels-Alder) |
| 18 | Amide formation | $\text{R}-\text{C}(=\text{O})-\text{Cl}$ + base (or anhydride) | "Schotten-Baumann" conditions |
| 19 | Diazonium salt formation | HNO ₂ , H ₂ SO ₄ (or NaNO ₂ , H ₂ SO ₄) | Can use NaNO ₂ and strong acid, which will make HNO ₂ |
| 20 | Chlorination (Sandmeyer) | CuCl | - |
| 21 | Bromination (Sandmeyer) | CuBr | - |
| 22 | Iodination | NaI (or KI) | Or KI |
| 23 | H ₂ O | H ₂ SO ₄ , H ₂ O, heat | can also use Cu ₂ O, H ₂ O |
| 24 | Cyanation (Sandmeyer) | CuCN | - |
| 25 | Fluorination | HBF ₄ | - |