Qualifying Exam Presentation

Proposal II:
Manipulating the Triplet State Lifetime of Fullerene-C60 Derivatives with Heterocycles

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Overview

I. Background
   A. Fullerene-C60 structure and properties
   B. Related chemistry, Diels-Alder reactions
   C. Architectural sensitivity
II. Heavy atom effect and triplet states
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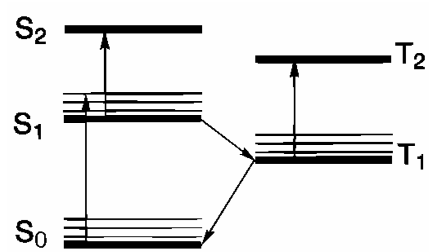
III. Synthesis
   A. Heterocyclic diene syntheses
   B. Fullerene derivative syntheses
IV. Characterization and evaluation
   A. NMR; mass spec.; elemental analyses; electrochemistry
   B. UV-Vis; fluorescence; phosphorescence
   C. Transient absorption experiments: triplet-triplet spectra; T-T extinction coefficients; triplet quantum yields

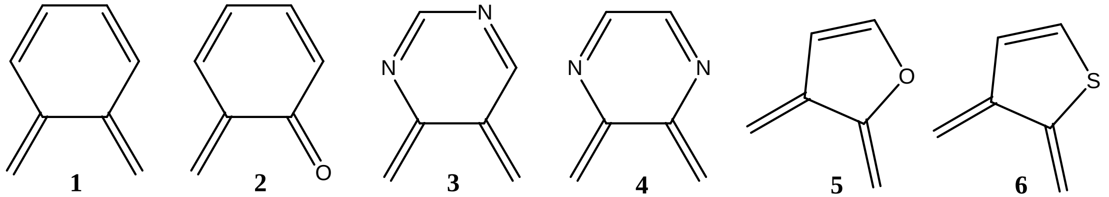
Structure and Properties

- Derivatization
  - 30 double bonds with similar reactivity
  - 6-6 double bonds at junctions of hexagons are dienophilic
- Photophysics
  - Intense absorptions in UV, weaker bands up to 700 nm
  - Short-lived S_1 state (low ns)
  - Long-lived T_1 state (10s – 100s μs)
  - Efficient energy transfer to oxygen to form $^1O_2$



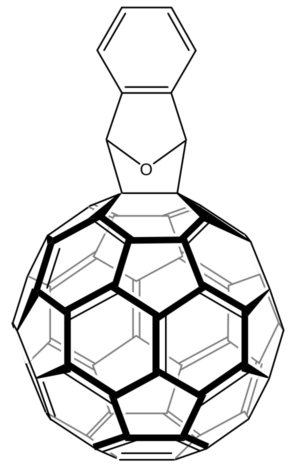
Energy level diagram for fullerenes

Related Chemistry, Diels-Alder



1 2 3 4 5 6

Series of o-quinodimethanes



Adduct with isobenzofuran

- Aromaticity gained by forming benzene and similar functionalities hinders retro-Diels-Alder.

Architectural Sensitivity

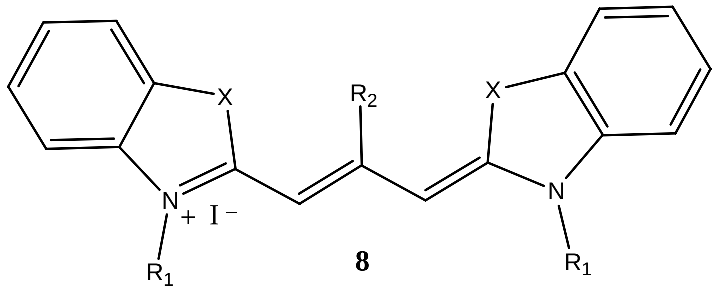
- Presence of alkoxy groups on far end of o-quinodimethanes makes little to no difference in photophysical properties.
- Functionalization of fullerene core reduces its photodynamic activity.
  - At least for adducts with O_2 and diethyl malonate.
- More than one addend reduces properties further.

- These facts led to the idea of using analogs of isobenzofuran.
  - Different heteroatoms in place of oxygen.
  - Variation in same space within two atom distance to fullerene core.

Heavy Atom Effect and Triplet States

- Increased atomic mass of heavy atom perturbs the magnetic field.
  - Allows for mixing of pure singlet and pure triplet states.
- This perturbation of the electronic system of the molecule facilitates intersystem crossing.
  - Rate of ISC increases.
- Subsequently, the rate of fluorescence decreases.

Heavy Atom Effect, Example



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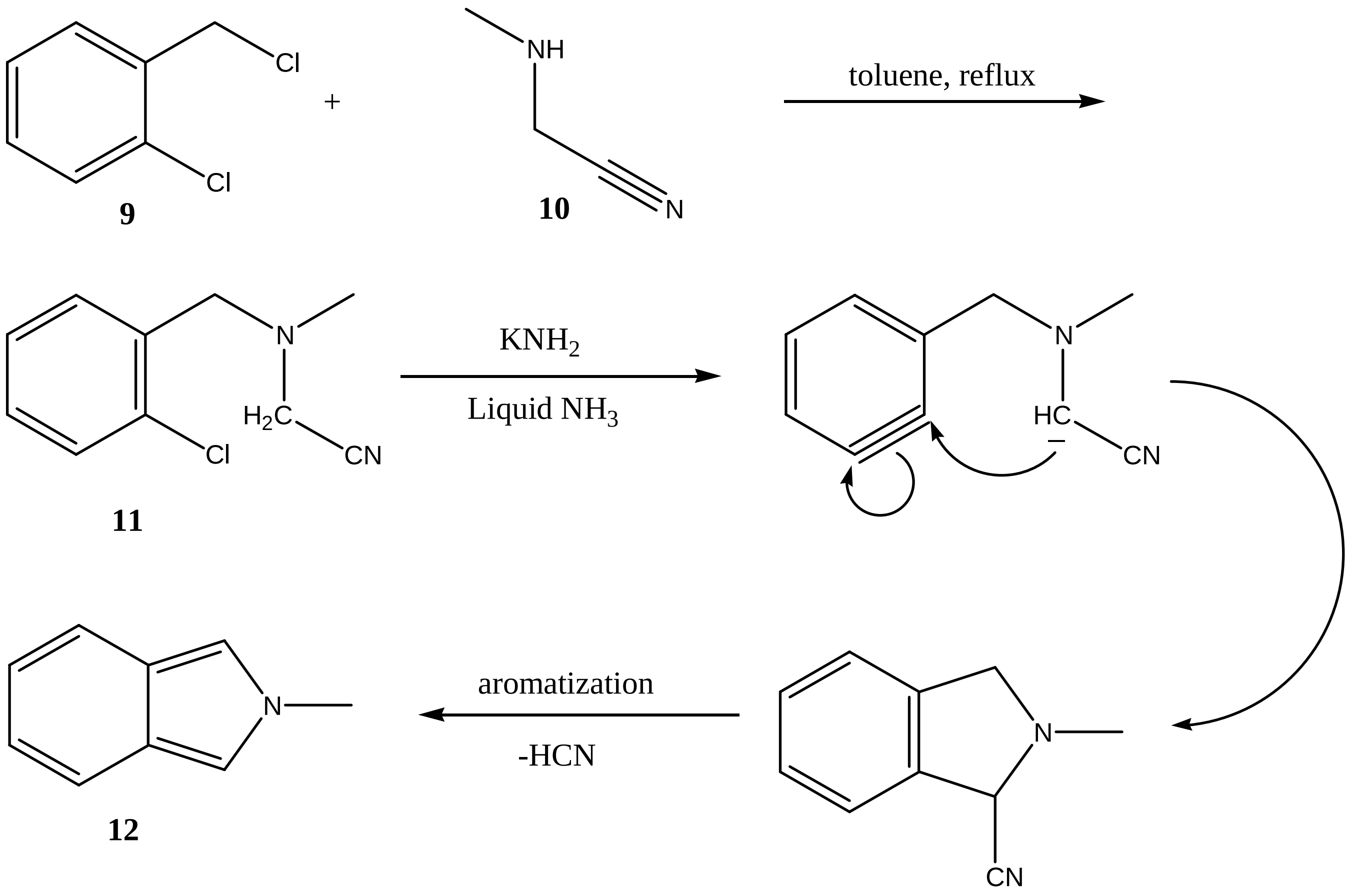
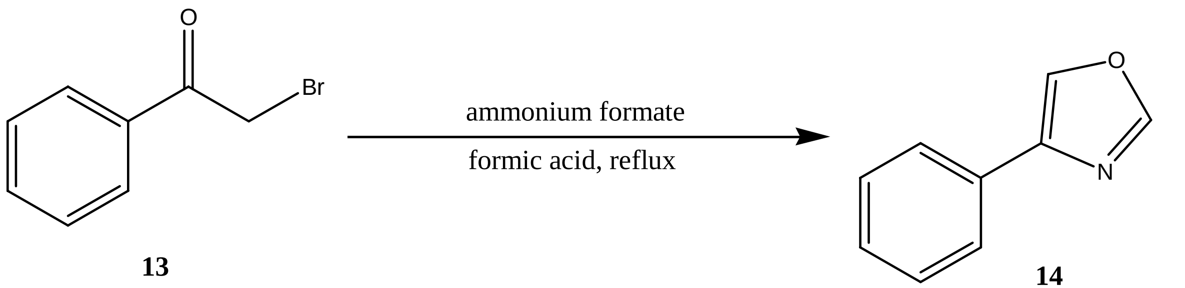
Dialkylcarbocyanine dyes, where X = S, Se; R1 = Et, Hex, Octodecyl; R2 = Me, Et, Ph.

- Quantum yield for ISC increased from less than 0.01 to 0.06.
- Quantum yield for singlet oxygen production increased from 0.001 to 0.014.
- Quantum yield for fluorescence decreased from 0.12 to 0.09.

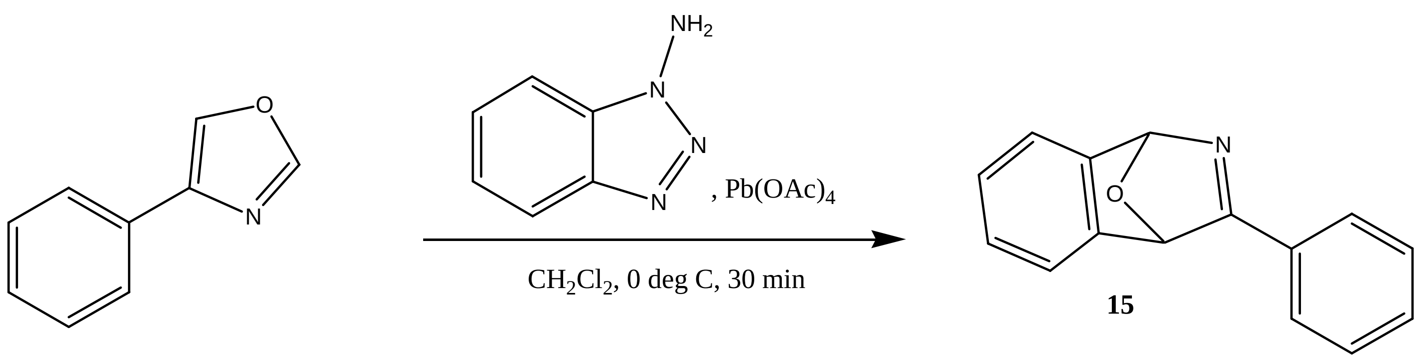
Diene Syntheses – 2-Methylisoindole



Diene Syntheses – Isobenzofuran



13 → 14



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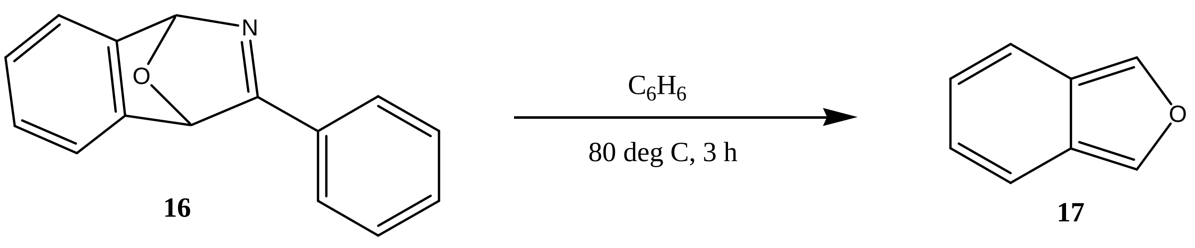
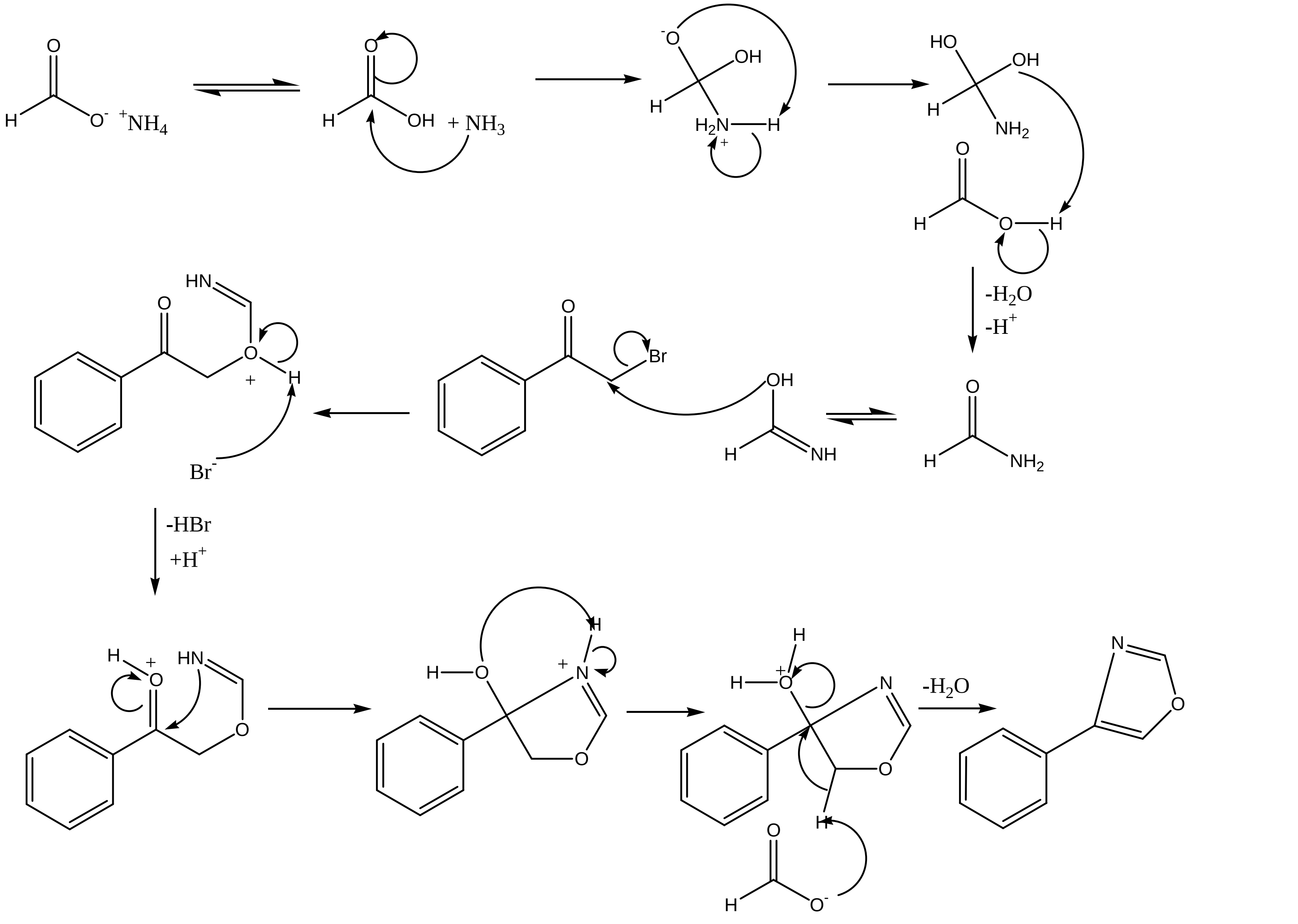
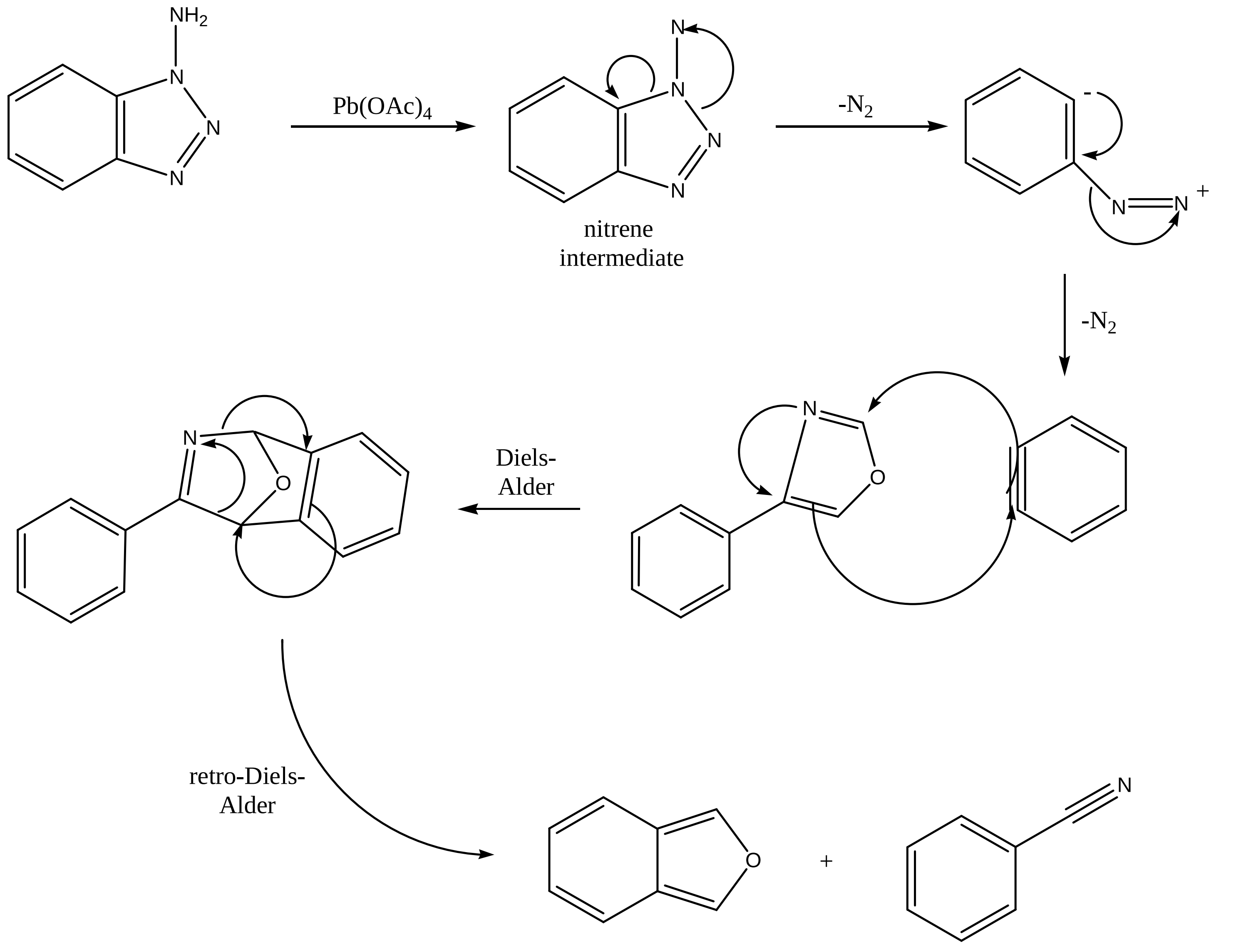


16 → 17

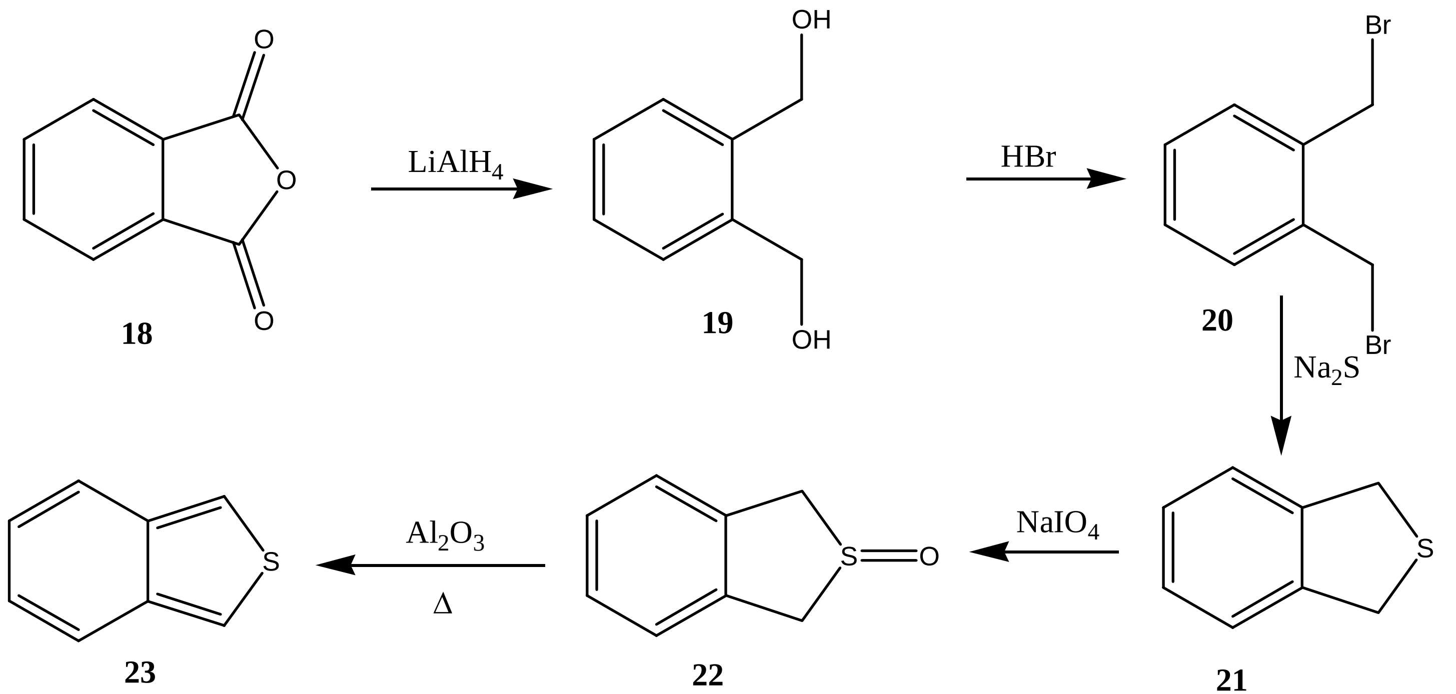
4-Phenyloxazole Synthesis



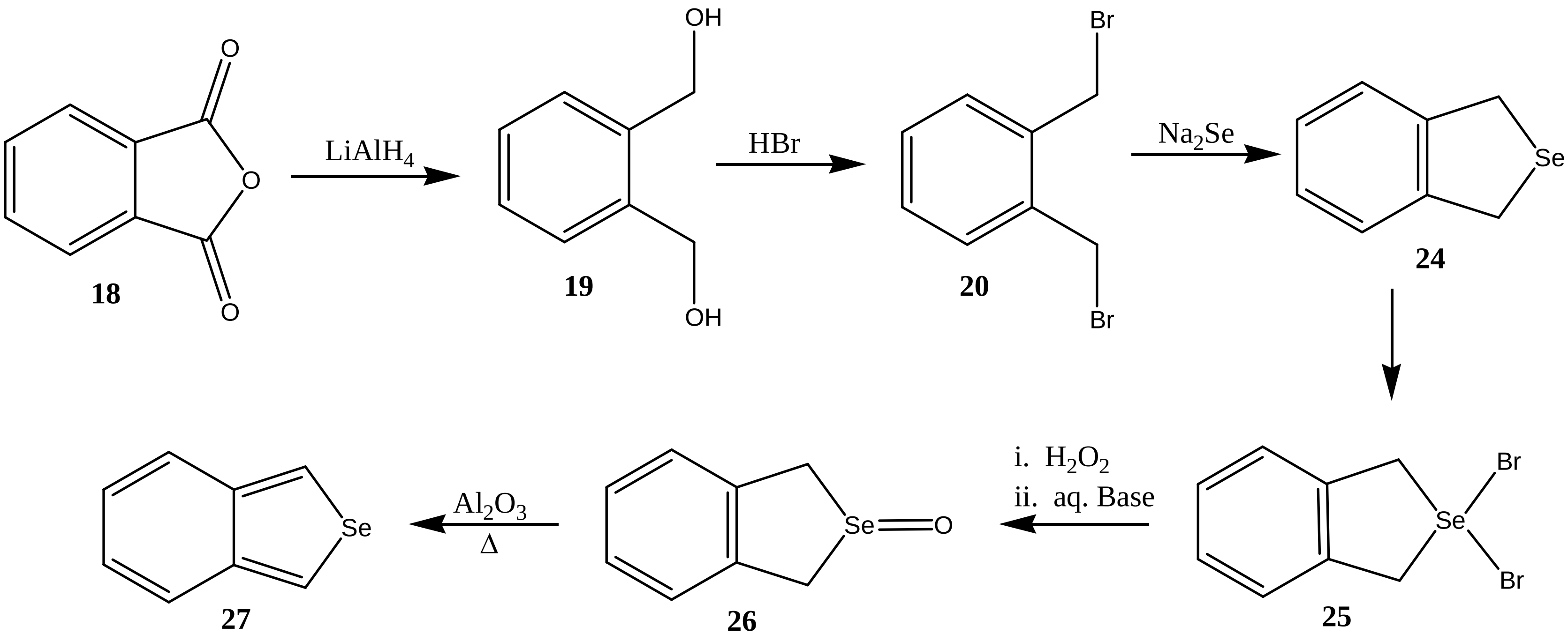
Reaction with 1-Aminobenzotriazole



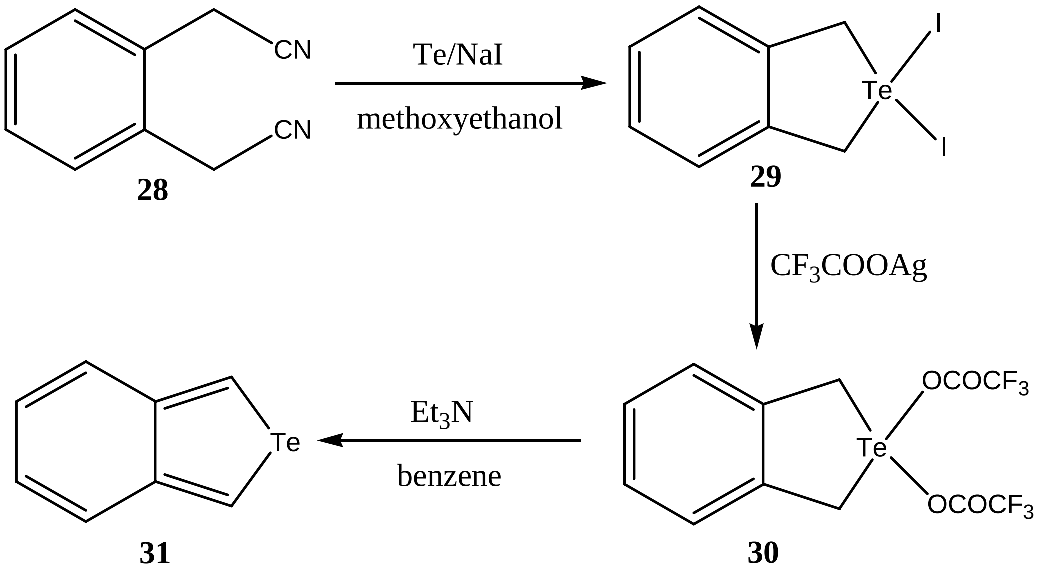
Diene Syntheses – Benzo[c]thiophene



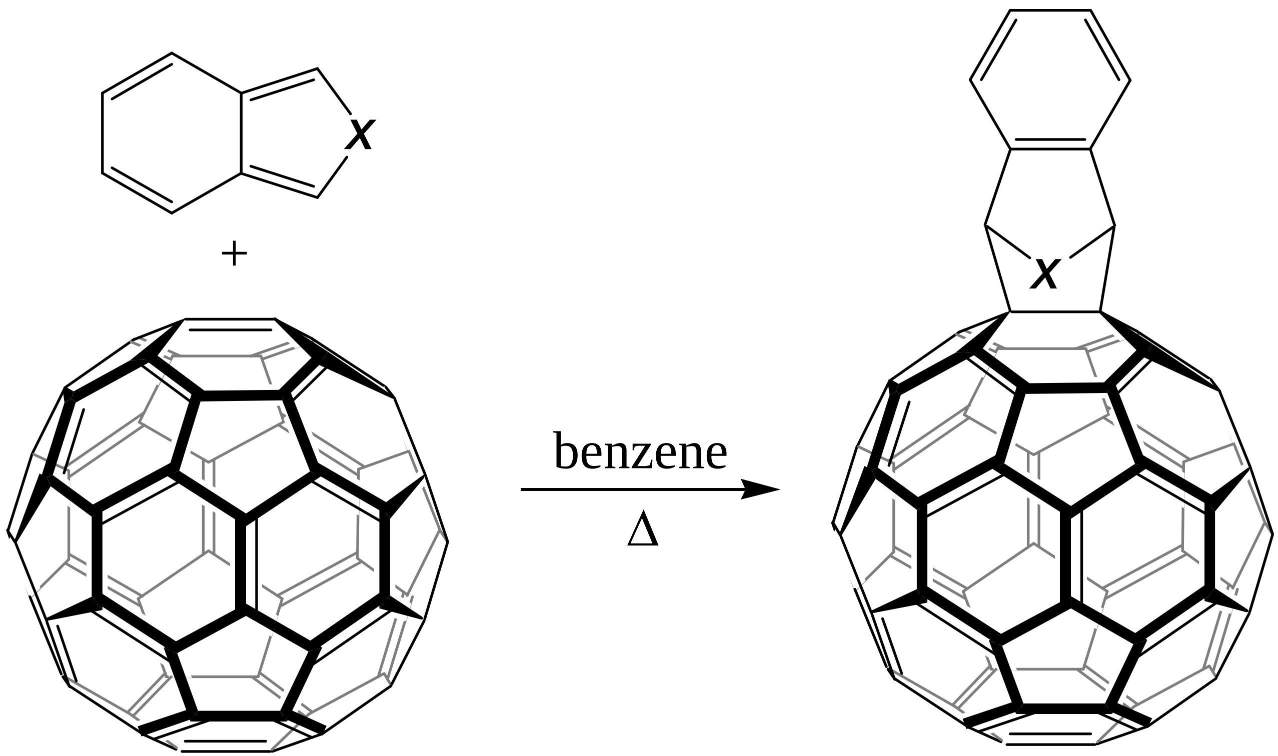
Diene Syntheses – Benzo[c]selenophene



Diene Syntheses – Benzo[c]tellurophene

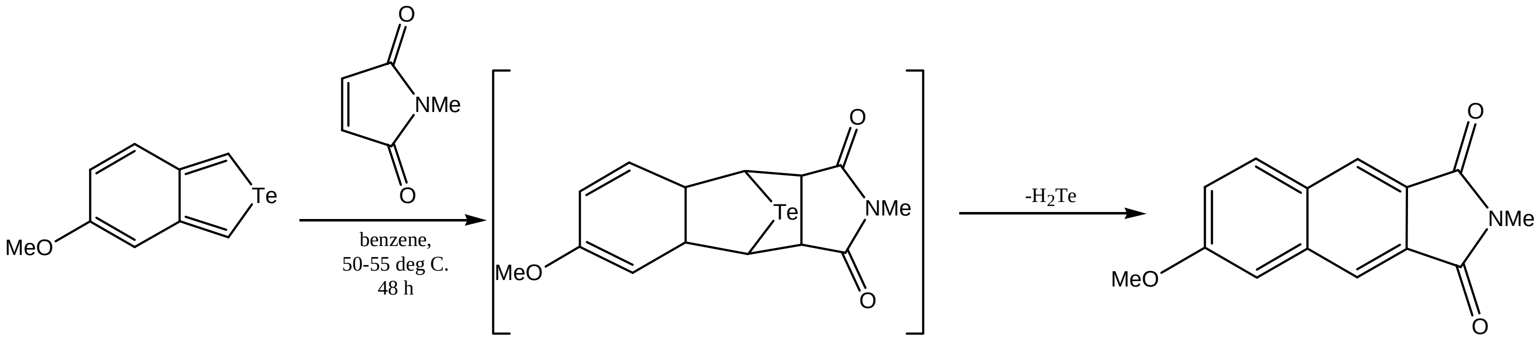


Fullerene Derivative Syntheses – Conventional Heating



[4 + 2] Diels-Alder reaction of heterocyclic diene with fullerene-C60, where *X* = N-CH3, O, S, Se, Te.

Fullerene Derivative Synthesis – Microwave Heating



- Intermediate was characterized by NMR, but proved to be unstable.

- Microwave heating with a short reaction time, with minimal but intense heating, may allow the tellurium compound to be synthesized.

Characterization and Evaluation

- ^{1}H, ^{13}C, ^{15}N, ^{77}Se, and $^{123/125}$Te NMR
- Mass spec.; elemental analyses; electrochemistry
- UV-Vis; fluorescence; phosphorescence
- Transient absorption experiments
  - Triplet-triplet spectra
  - Triplet-triplet extinction coefficients
  - Triplet quantum yields
  - Triplet energies
- Near-infrared emission spectra

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