Hypervalent Iodine(III) Chemistry

Structure and properties of λ³ iodanes
- distorted trigonal pyramids
- 3-centre-4-electron bond (I 5p orbital)
  \[ \overset{\delta^-}{R} \text{I} \overset{\delta^+}{X} \]
  → long, weak, highly polarised bond
  → very reactive compounds
- “Hypernucleofuge”: leaving group ability of PhI in Ph(R)I⁺X⁻ 10⁶ times greater than OTf⁻
- Stability: R = (Het)Ar: isolable, shelf-stable; R = alkyl: unstable towards reductive α/β-elimination, homolytic R-I bond cleavage, nucleophilic attack (add steric bulk or strongly electron withdrawing groups to stabilise)


Reactivity I: Oxidants
Q1  Provide mechanism and product for the following reaction:

Based on previous work by: R. Criegee, H. Beucker, Justus Liebigs Annalen der Chemie 1939, 541, 218.
Q2 Propose a mechanism for the following transformation. What is the name of this reaction? (Hofmann Rearrangement)


Reactivity II: Reaction with Nucleophiles
- “hypernucleofuge” → very strong electrophiles
- reaction with nucleophiles may occur via radical or ionic mechanism (depending on nature of nucleophile)

\[
\text{Ar}_2^+X^- + \text{Nu} \xrightarrow{\text{radical}} [\text{Ar}_2^+] \xrightarrow{\text{Ar}^+ + \text{Ar}^-} \text{Ar-Nu} \quad \text{(e.g. BuLi, PPh}_3, \text{OH}^-, \text{Hg, Py)}
\]

\[
\text{Ar}_2^+X^- + \text{Nu} \xrightarrow{\text{ionic}} \text{Ar-Nu} + \text{ArI} \quad \text{(e.g. N}_3^-, \text{SCN}^-, \text{PhCO}_2^-, \text{Br}^-, \text{Cl}^-)
\]
Q3 Propose a mechanism and product for the following reaction:

$$\begin{align*}
\text{O} & \quad \text{H} - \text{C} - \text{Ph} + \text{CF}_3^+ - \text{I} - \text{O} => \text{H} - \text{O} - \text{CF}_3 \\
\text{H} - \text{C} - \text{Ph} & \quad \text{Togni's reagent}
\end{align*}$$

Togni's reagent

In the paper, the authors propose the following ionic mechanism:


Since then, mechanistic studies by Buchwald, Sanford, Wang, Yu and others have shown that in the presence of a single-electron reductant such as Cu(I), CF$_3^+$ is reduced to the trifluoromethyl radical, thus postulating a radical mechanism.

Reactivity III: Cross-Coupling Chemistry

Q4 Propose a mechanism for the following cross-coupling reaction:

$$\text{EtO}_2\text{C} \rightleftharpoons \text{Ph}$$