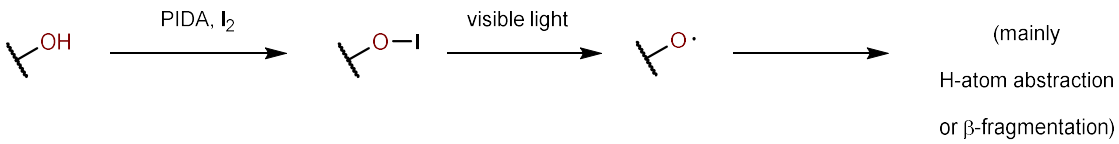
Suàrez Radical Formation

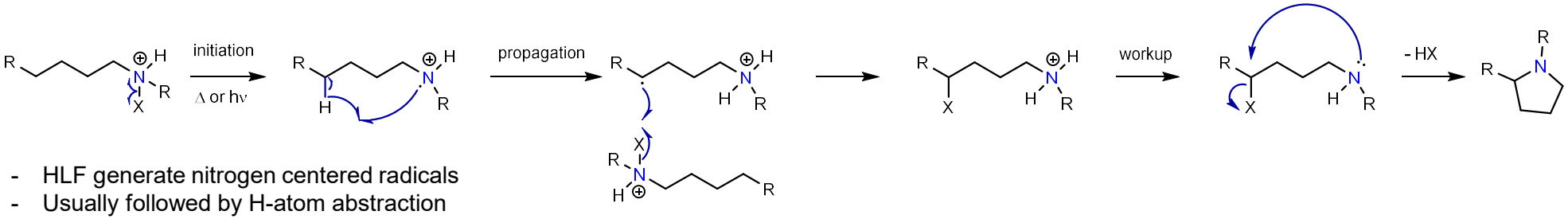
Introduction:



- Method for the formation of oxygen centered radical
- Mild conditions
- Possible different products depending on the reactivity of the intermediate

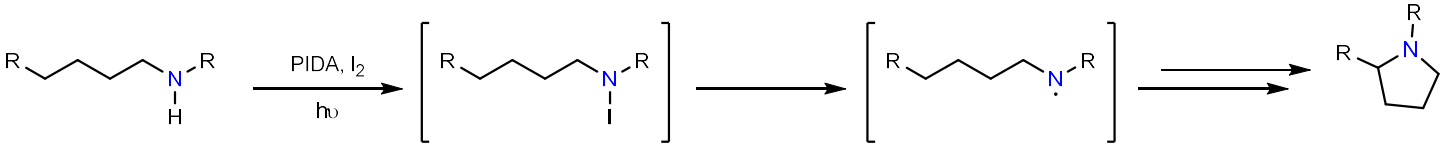
Historical perspective:

Hofmann-Loeffler-Freytag Reaction



- HLF generate nitrogen centered radicals
- Usually followed by H-atom abstraction

Suàrez modification (1980)



- Suàrez discovered milder conditions
- Initial work on irradiation of nitroamines with $Pb(OAc)_4$ and I_2
- Mixture of PIDA and I_2 under visible light irradiation

Suàrez, E *J. Chem. Soc., Chem. Commun.* **1980**, 958-959. https://doi.org/10.1039/C39800000958

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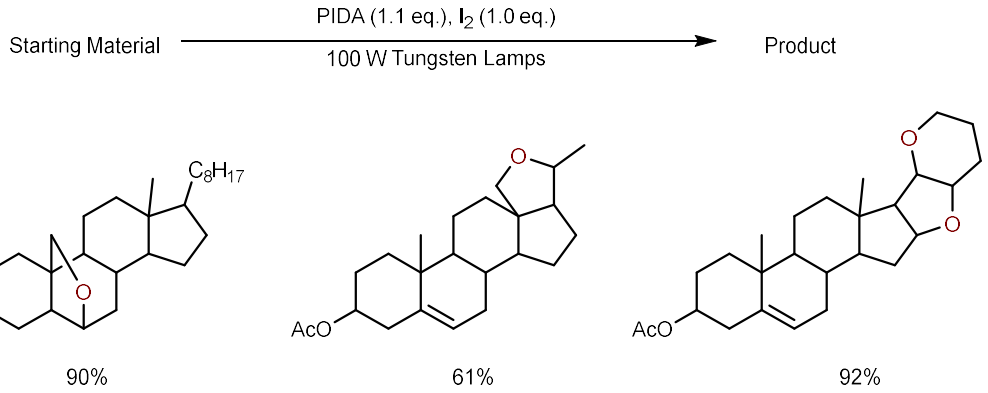
Development of the method (1984):

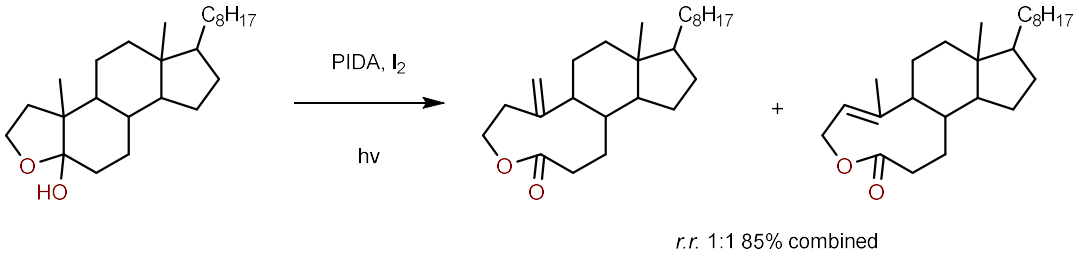
INTRAMOLECULAR HYDROGEN ABSTRACTION. IODOSOBENZENE DIACETATE, AN EFFICIENT AND CONVENIENT REAGENT FOR ALKOXY RADICAL GENERATION

José I. Concepción, Cosme G. Francisco, Rosendo Hernández, José A. Salazar, and Ernesto Suárez*



- It was noted that same conditions could be applied for oxygen
- Scope presented limited to specific family of substrates
- Catalytic amounts of I_2 could be used with longer reaction times.

Suàrez, E. *Tetrahedron Letters* **1984,** *25* , 1953-1956. https://doi.org/10.1016/S0040-4039(01)90085-1

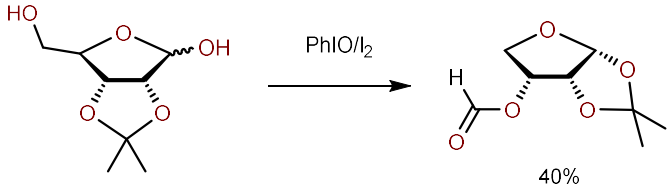


r.r. 1:1 85% combined

- Second paper published 2 years later
- Specific cases of β-fragmentation were reported
- Reaction proceeds through the corresponding iodide, followed by elimination.

Suàrez, E. *Tetrahedron Letters* **1986**, *27* (3), 383-386. https://doi.org/10.1016/S0040-4039(00)84025-3

- In 1993 paper on β-fragmentation on sugar derivatives
- Method then widely used for this type of rearrangement
- Slight modifications to the conditions (PhIO instead of PIDA and no light required).



Suàrez, E. *J. Am. Chem. Soc.* **1993**, 115, 8865-8866. https://doi.org/10.1021/ja00072a060

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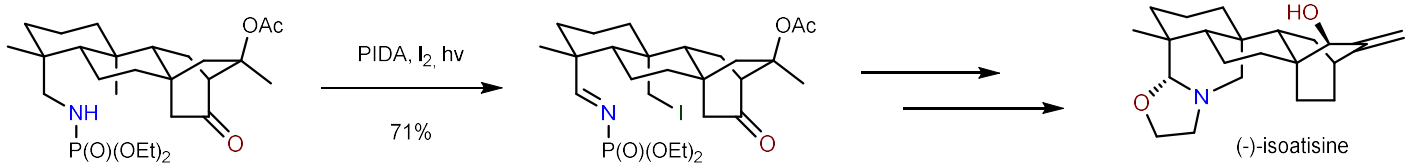
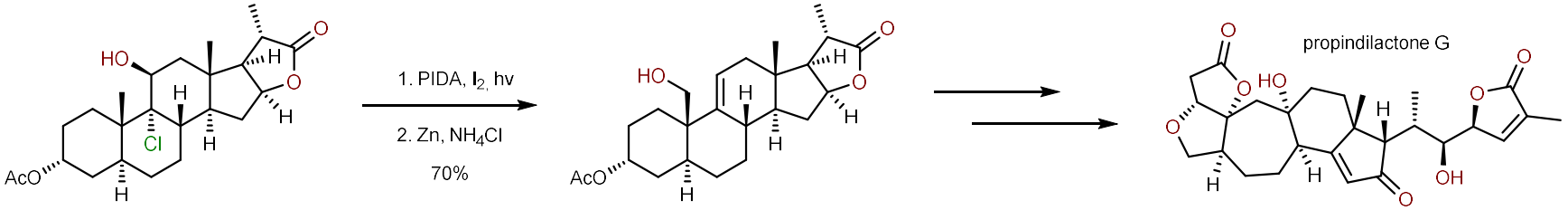
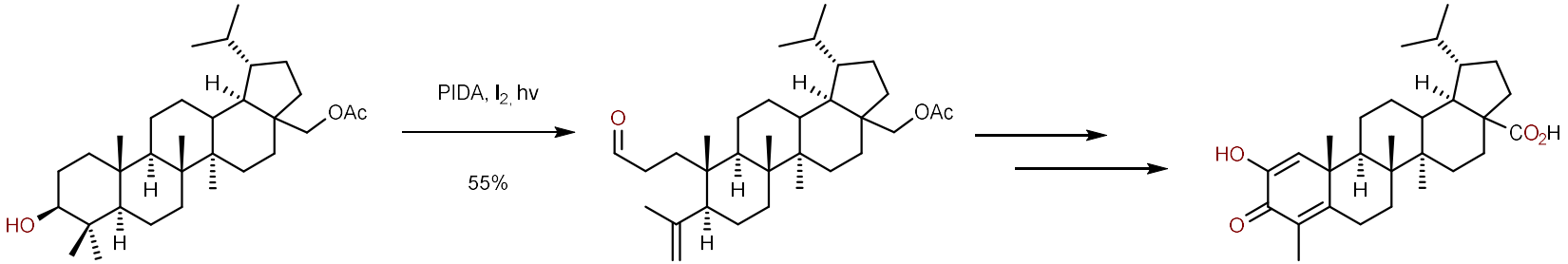
Applications to synthesis:



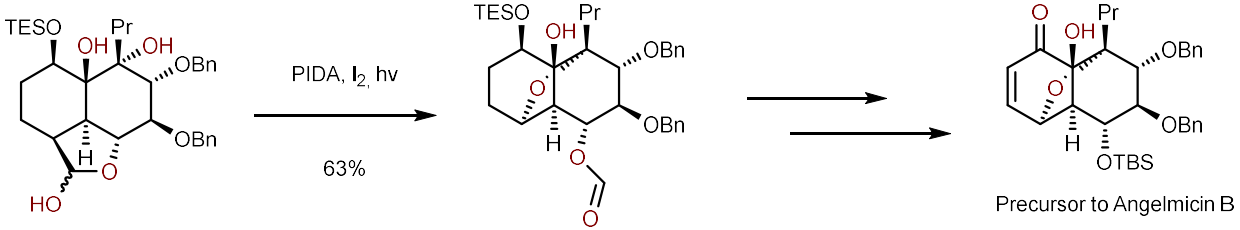
Baran, P.S. *J. Am. Chem. Soc.* **2014**, 136, 12592−12595. https://doi.org/10.1021/ja507321j



Gui, J. *J. Am. Chem. Soc.* **2020**, 142, 5007−5012. https://doi.org/10.1021/jacs.0c00363



Snyder, J. K. *J. Org. Chem.* **2002**, 67, 2864-2873. https://doi.org/10.1021/jo010929h



Mootoo, D. R. *Eur. J. Org. Chem.* **2011**, 6281–6287. https://doi.org/10.1002/ejoc.201100815

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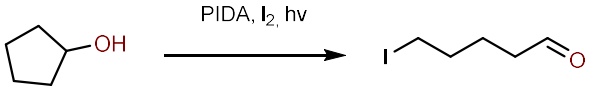
Mechanisms:

- In 1994 work in which hypoiodite specie were spectroscopically detected
- Confrontation by confrontation with other hypoiodites obtained by other methods. ($AgOAc + I_2$)

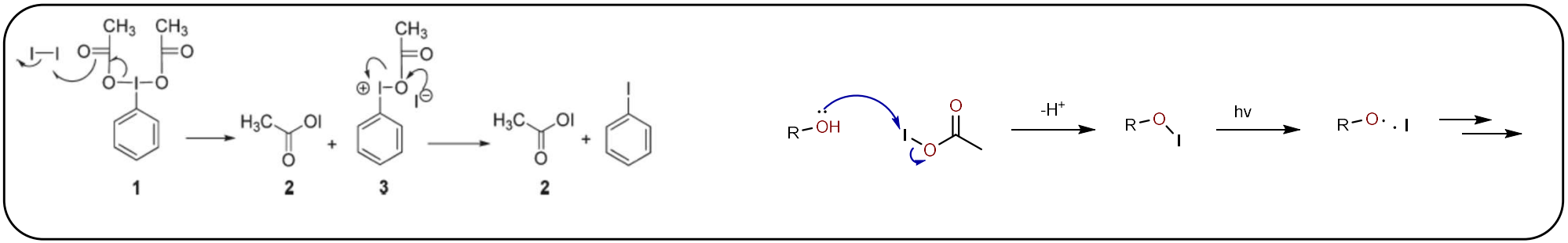


Detected species:

Pagè, D. *Tetrahedron Letters.* **1994,** 35(7), 1003-1006. https://doi.org/10.1016/S0040-4039(00)79950-3

Proposed mechanism with PIDA:

- From 1 eq. of PIDA 2 eq. of iodosoacetate are formed
- In theory 0.5 eq. of iodine are required
- This is in contrast with original conditions reported by Suàrez (0.3 eq. of I_2)



- Actually, things are more complex because there are other decomposition pathways of PIDA that must be considered.

Vinod, T. K. *J. Org. Chem.* **2011**, 76, 974–977. https://doi.org/10.1021/jo102051z

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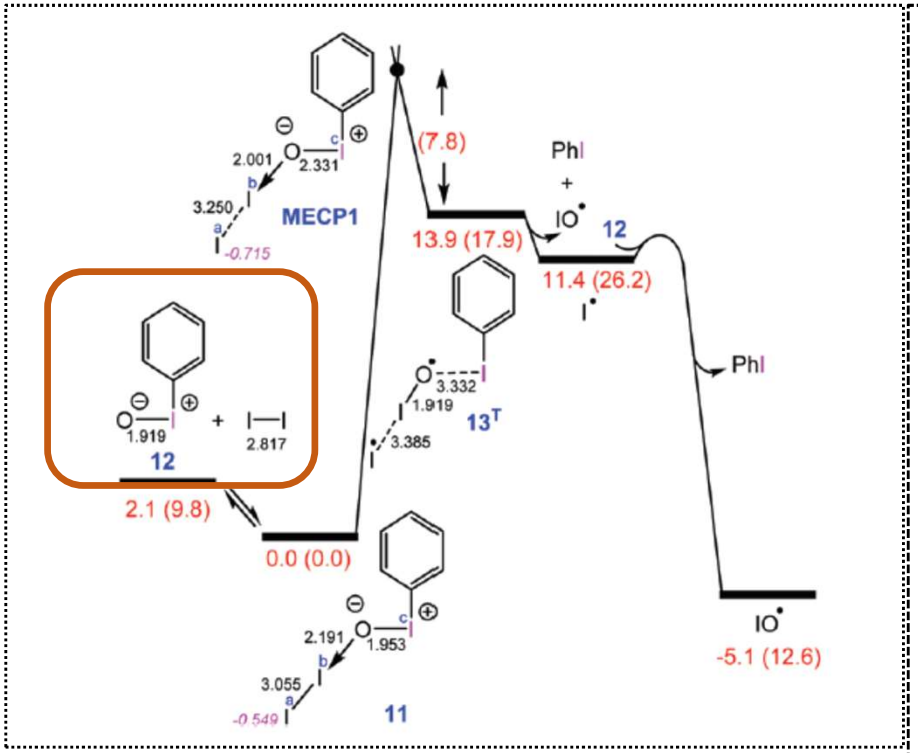
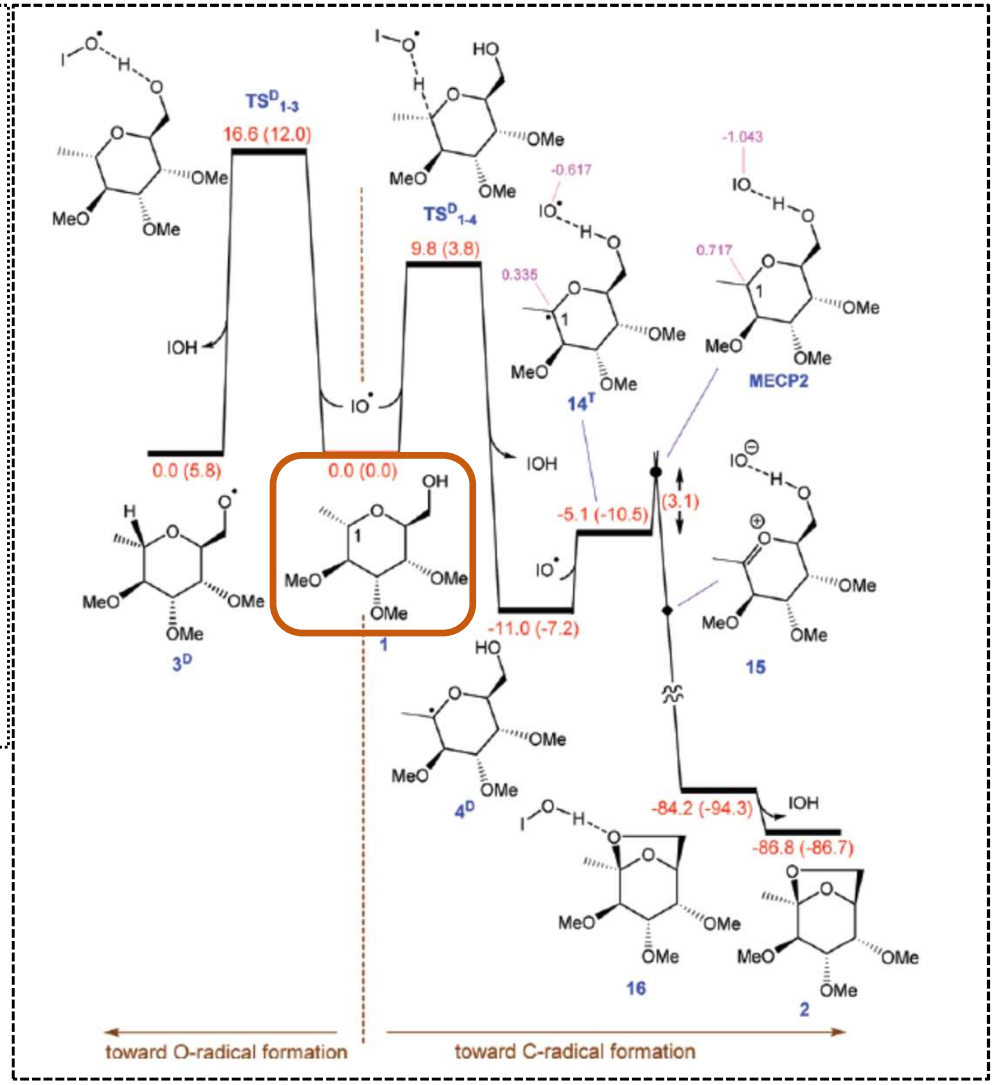
Proposed mechanism with PhIO:





- With iodosobenzene a computational study suggests the mechanism proceeds through a double radical abstraction
- Two ISCs could be involved.
- This can be rationalized thanks to the lower energetic barrier of such process compared to the “classic” Suarèz mechanism.
- Light is not taken into consideration.

Ariafard, A. *Org. Biomol. Chem.* **2020**, 18, 8103. https://doi.org/10.1039/D0OB01705A