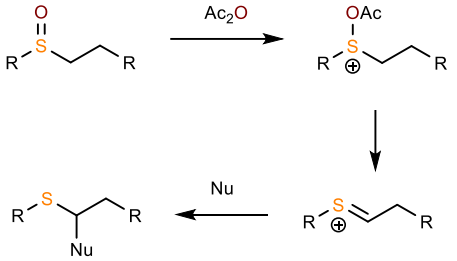
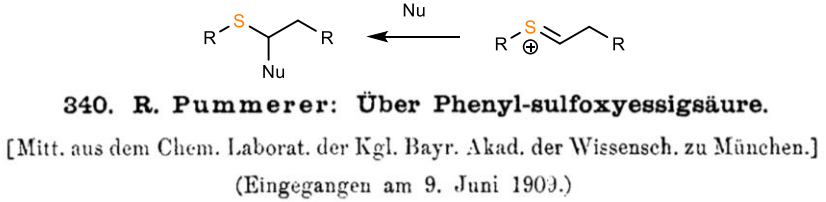
# Pummerer Rearrangement

## Introduction

- Pummerer rearrangement was first reported in 1909 by Rudolph Pummerer.
- Typically, a sulfoxide is activated with an anhydride such as $Ac_2O$ or TFAA.
- Elimination of this group generates a thionium which can be trapped by a nucleophile
- The most common application that is seen in total synthesis is trapping of the thionium with –OAc or –OTFA which upon hydrolysis affords an aldehyde.



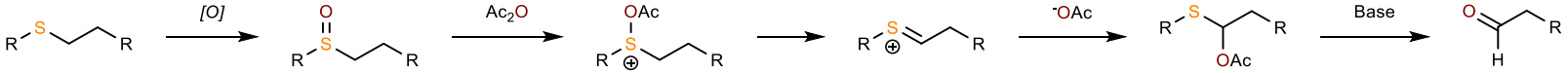
340. R. Pummerer: Über Phenyl-sulfoxyessigsäure.

[Mitt. aus dem Chem. Laborat. der Kgl. Bayr. Akad. der Wissensch. zu München.]

(Eingegangen am 9. Juni 1909.)

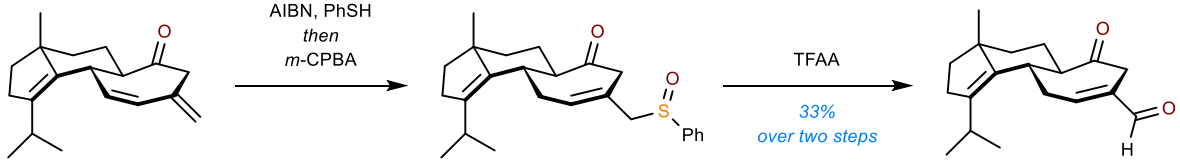

Pummere, P. *Ber. Dtsch. Chem. Ges*. **1909**, 42, 2282. https://doi.org/10.1002/cber.190904202126
Procter, D. *Angew. Chem. Int. Ed*. **2010**, 49, 5832-5844. https://doi.org/10.1002/anie.201000517
Padwa, A. *Angew. Chem. Rev.* **2004**, 104, 2401-2432. https://doi.org/10.1021/cr020090l


## Pummerer Rearrangement to Form Carbonyls

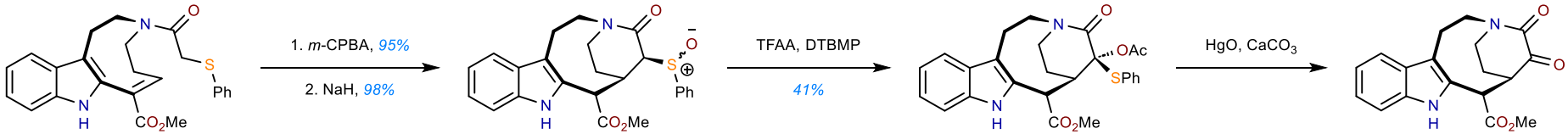



- Many examples in total synthesis bring the sulfide in by $S_N2$, Mitsunobu, or hydrothiolation. The sulfide is then oxidized to the corresponding sulfoxide.
- Acetate or trifluoroacetate are the most commonly used nucleophiles when utilizing the Pummerer rearrangement to prepare aldehydes.

## Examples in Total Synthesis




Li, Y. *J. Am. Chem. Soc.* **2024**, 146, 25078–25087. https://doi.org/10.1021/jacs.4c08042



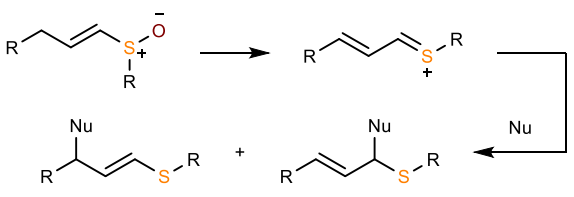

Magnus, P. *J. Am. Chem. Soc.* **1993**, 115, 8116-8129. https://doi.org/10.1021/ja00071a025

# Pummerer Rearrangement

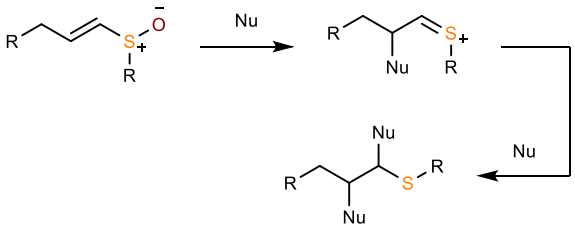


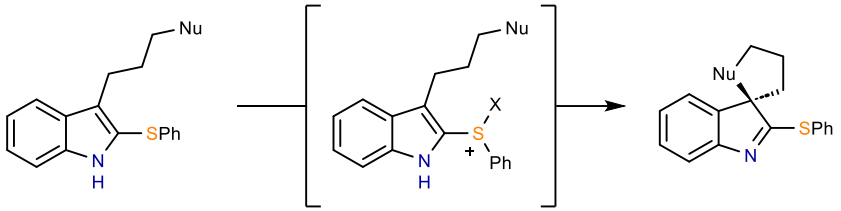
## Vinylogous Pummerer Rearrangement

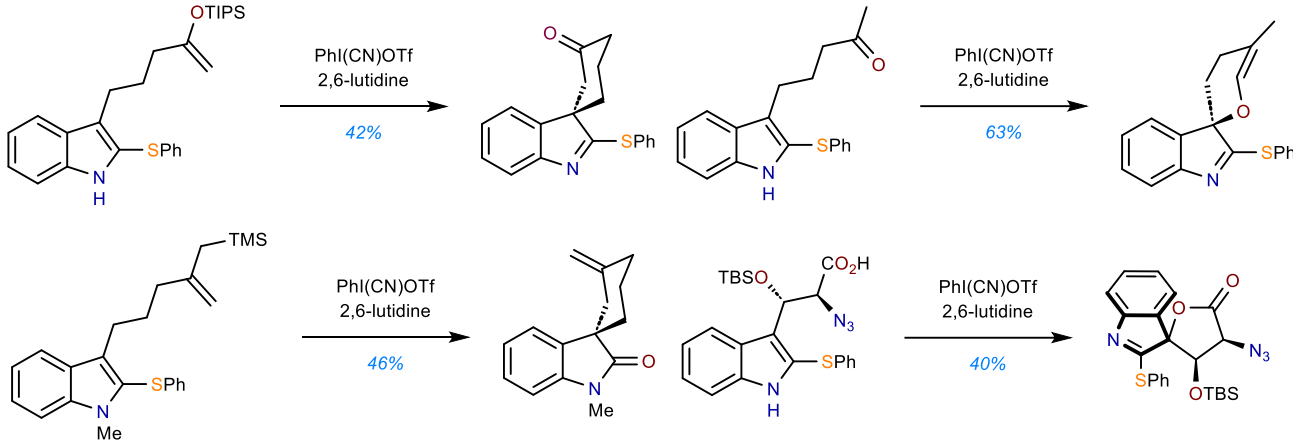
*Vinylogous Pummerer*



*Additive Pummerer*

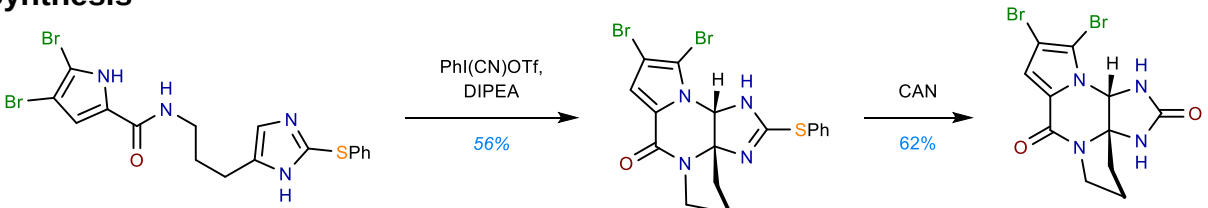






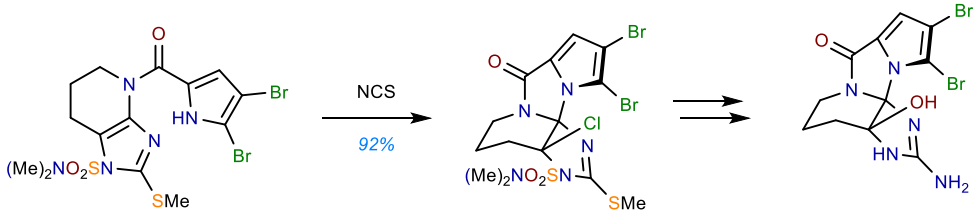

Feldman, K. *Tetrahedron Lett.* **2004**, 45, 5035-5037. https://doi.org/10.1016/j.tetlet.2004.04.182
Feldman, K. *J. Org. Chem.* **2005**, 70, 6429-6440. https://doi.org/10.1021/jo050896w

## Applications in Total Synthesis




Feldman, K. *Org. Lett.* **2005**, 7, 929-931 https://doi.org/10.1021/ol0500113

*dibromophakellstatin*



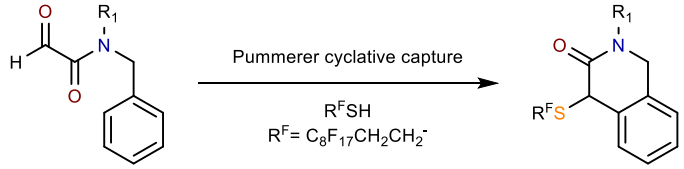

*(±)-dibromoagelaspongin*

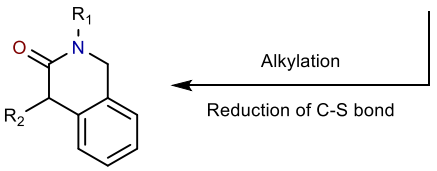
Feldman, K. *J. Am. Chem. Soc.* **2008**, 130, 14964-15965 https://doi.org/10.1021/ja807020d

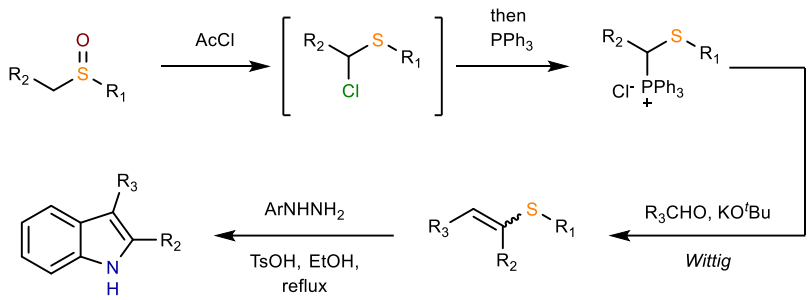
# Pummerer Rearrangement

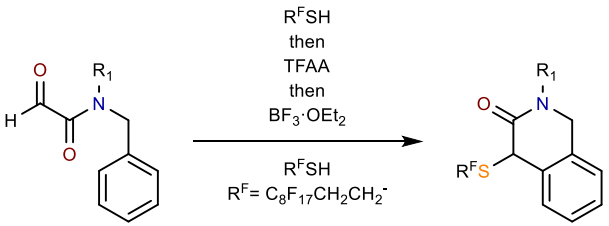


## Heterocycle Synthesis

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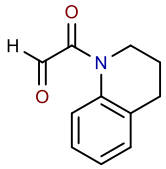
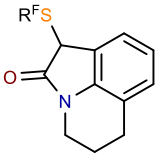
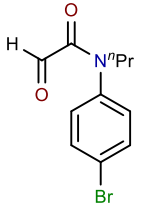
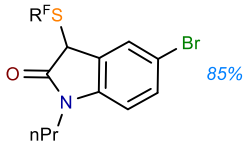
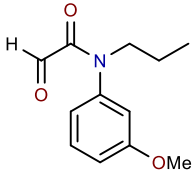
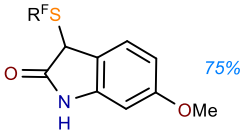
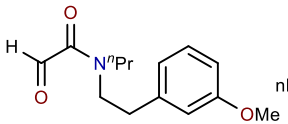
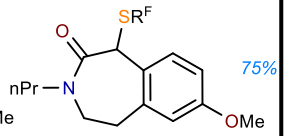
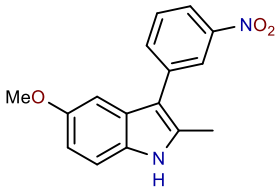
|---|---|---|---|---|---|
|  |  | 65% |  |  | 85% |
|  |  | 75% |  |  | 75% |

Procter, D. *Angew. Chem. Int. Ed.* **2005**, 2, 1165-1168. https://doi.org/10.1021/ol005777b
Magolan, J. *Synthesis.* **2022**, 54, 4917-4931. 10.1055/a-1868-4148

*Indoles*

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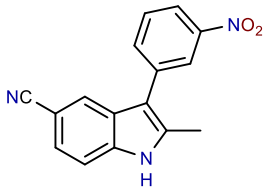


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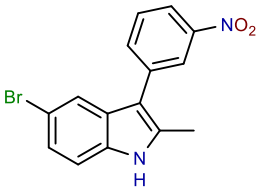


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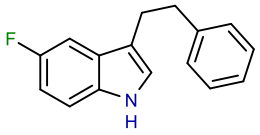


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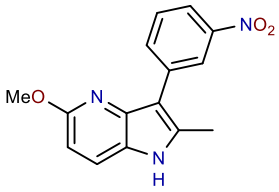


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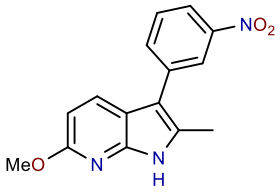


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