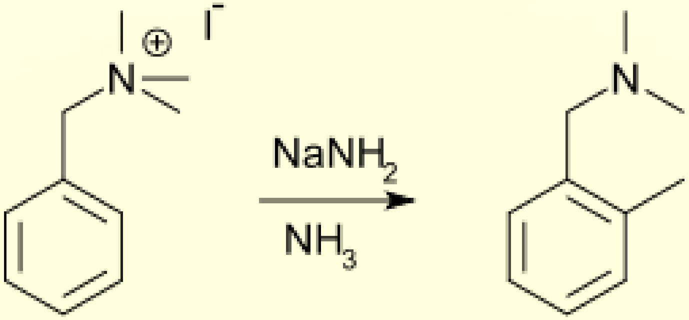
SOMMELET-HAUSER REARRANGEMENT

2018-11-13

WZQ

Sommelet–Hauser rearrangement

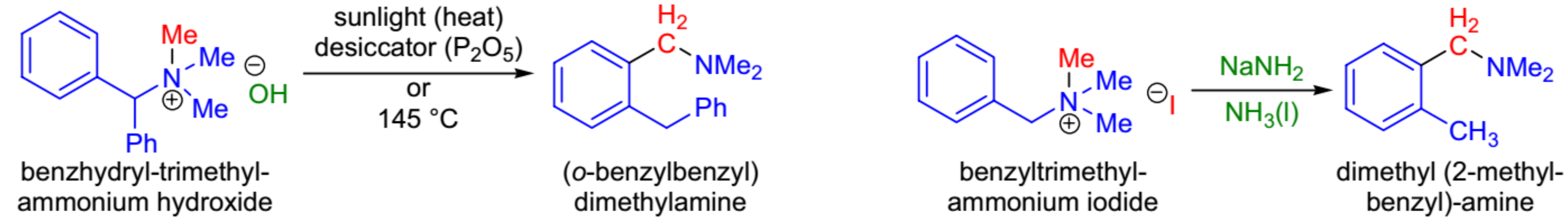


- The Sommelet–Hauser rearrangement (named after M. Sommelet and Charles R. Hauser) is a rearrangement reaction of certain benzyl quaternary ammonium salts.
- The reaction product a N,N-dialkylbenzylamine with a new alkyl group in the aromatic ortho position.

Sommelet–Hauser rearrangement

Sommelet (1937):

Hauser (1951):



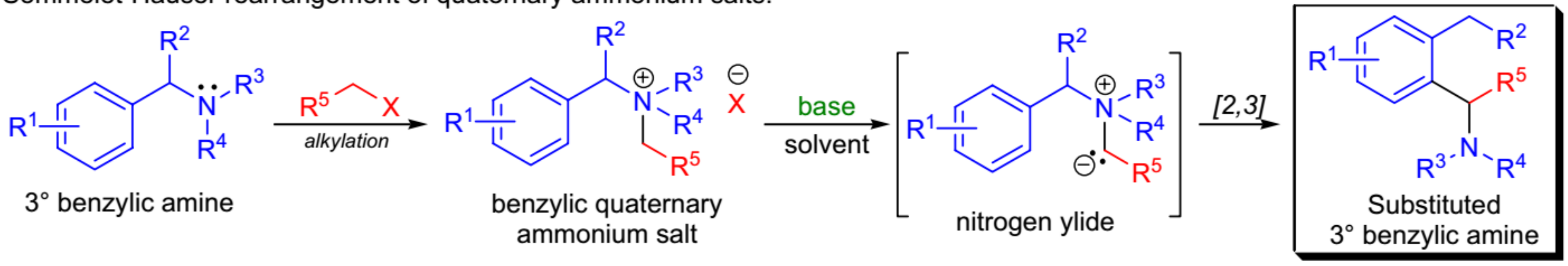
benzhydryl-trimethyl-ammonium hydroxide

(*o*-benzylbenzyl) dimethylamine

benzyltrimethyl-ammonium iodide

dimethyl (2-methyl-benzyl)-amine

Sommelet-Hauser rearrangement of quaternary ammonium salts:



3° benzylic amine

benzylic quaternary ammonium salt

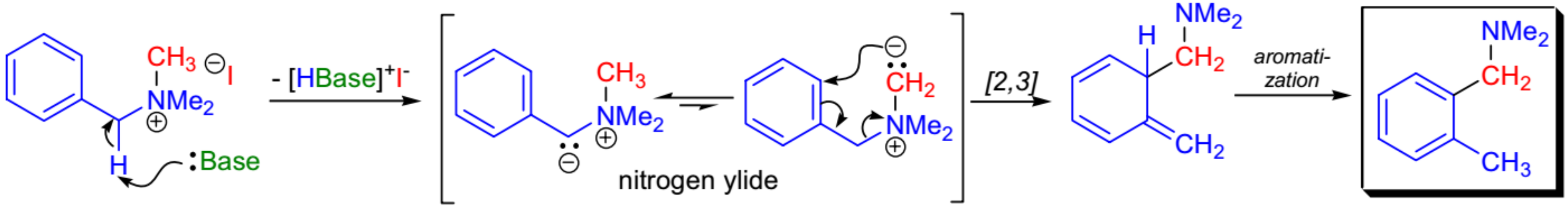
nitrogen ylide

Substituted 3° benzylic amine

R^1 = usually EDG = H, alkyl, aryl, *O*-alkyl; R^2 = H, alkyl, aryl; $R^{3\text{-}4}$ = CH_3, alkyl with no β-hydrogen, aryl; R^5 = most often H, 3° alkyl; X = Cl, Br, I; base = $NaNH_2$, KNH_2, alkyllithium; solvent = NH_3 (liquid), DMSO, HMPA

Sommelet–Hauser rearrangement

Mechanism: [21-25]



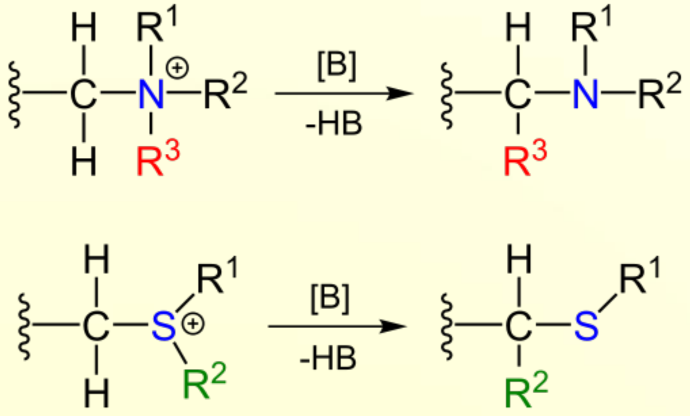
Features：

1. when there are two possible sites of deprotonation, usually the more stableylide is formed (derived from the more stable carbanion).
2. when it is not possible to form the ylide by deprotonation because the initial benzylic carbanion is significantly stabilized (e.g., R1=EWG group such as CN, NO2, Cl, Br), the rearrangement may not occur;
3. when the alkyl groups attached to the nitrogen contain a hydrogen atom at their β-position, the Hofmann elimination may compete; cyclic quaternary ammonium salts react by ring-expansion
4. One major competing reaction is the Stevens rearrangement; in systems where both the Stevens- and S.-H. rearrangements are possible, the choice of reaction conditions allow control over which of these competing processes dominate;

Sommelet–Hauser rearrangement

Competing reactions：

Stevens rearrangement:

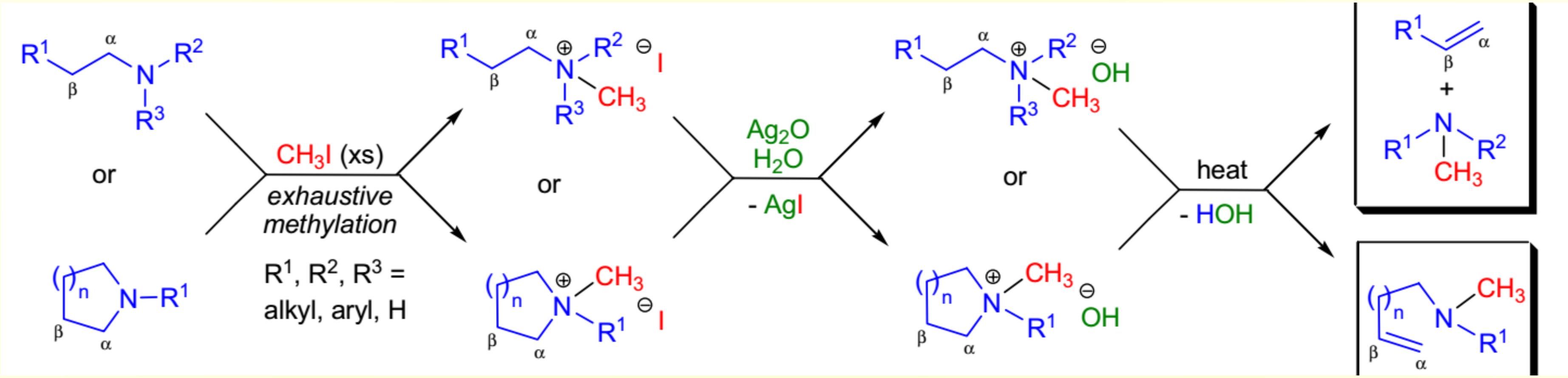


low temperatures and polar solvents (e.g., NH3, DMSO, HMPA) usually favor the S.-H. rearrangement, whereas higher temperatures and nonpolar solvents (e.g., hexanes, ether) facilitate the Stevens rearrangement;

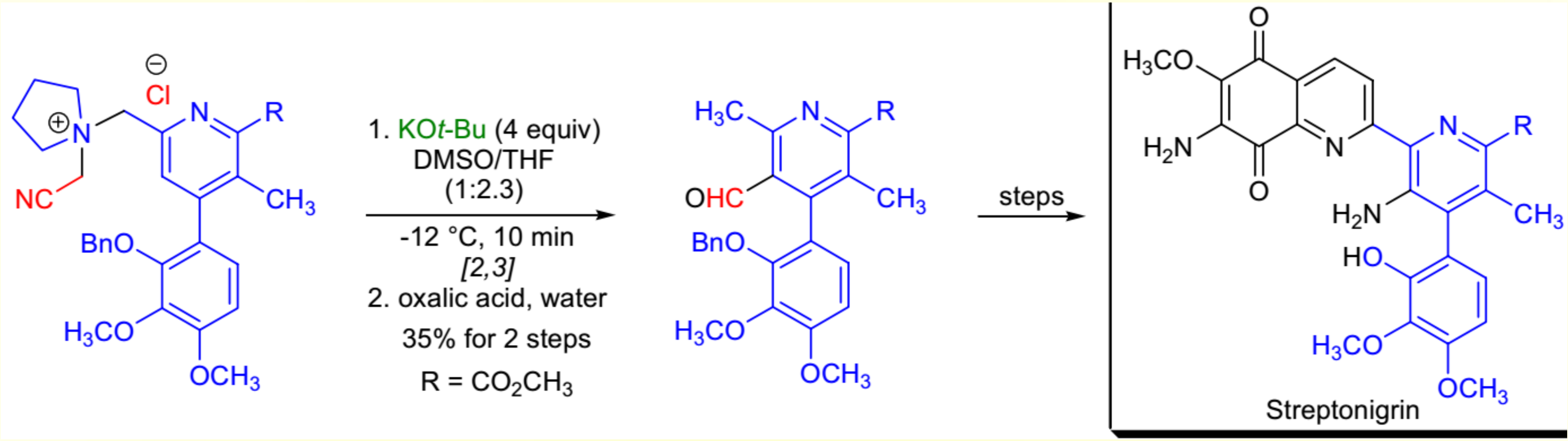
Sommelet–Hauser rearrangement

Competing reactions：

Hofmann elimination:

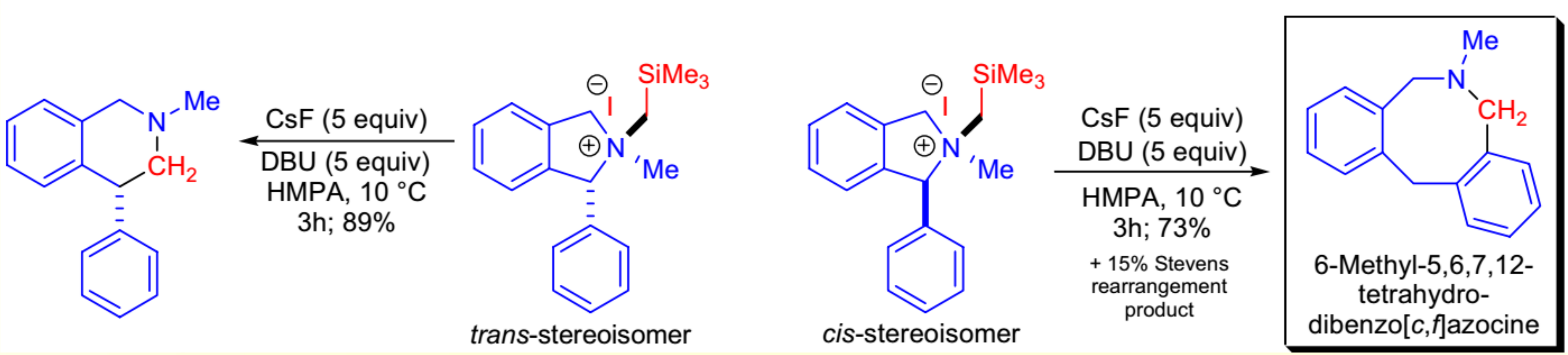


Sommelet–Hauser rearrangement



Sommelet–Hauser rearrangement

The generation of nitrogen ylides is possible under neutral conditions by fluoride-induced desilylation of (trimethylsilyl)methyl ammonium halides.



Sommelet–Hauser rearrangement

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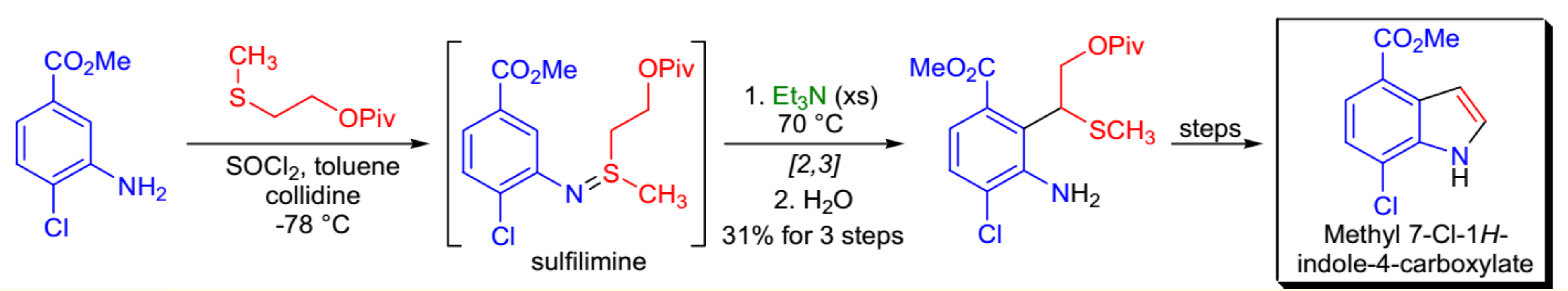
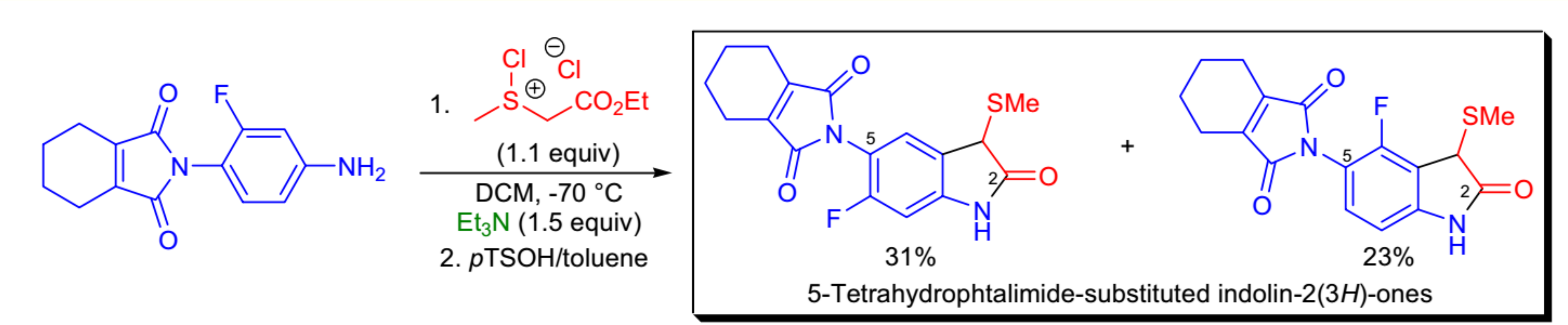


sulfilimine

Methyl 7-Cl-1*H*-indole-4-carboxylate



5-Tetrahydrophtalimide-substituted indolin-2(3*H*)-ones