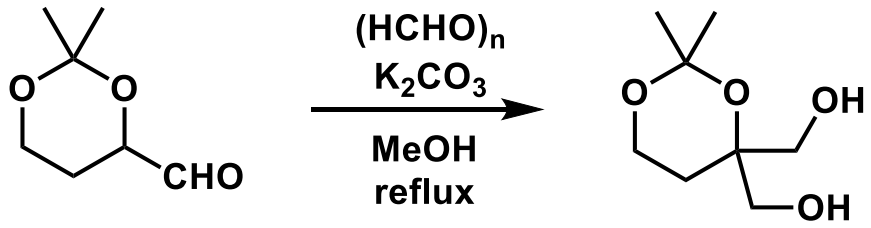
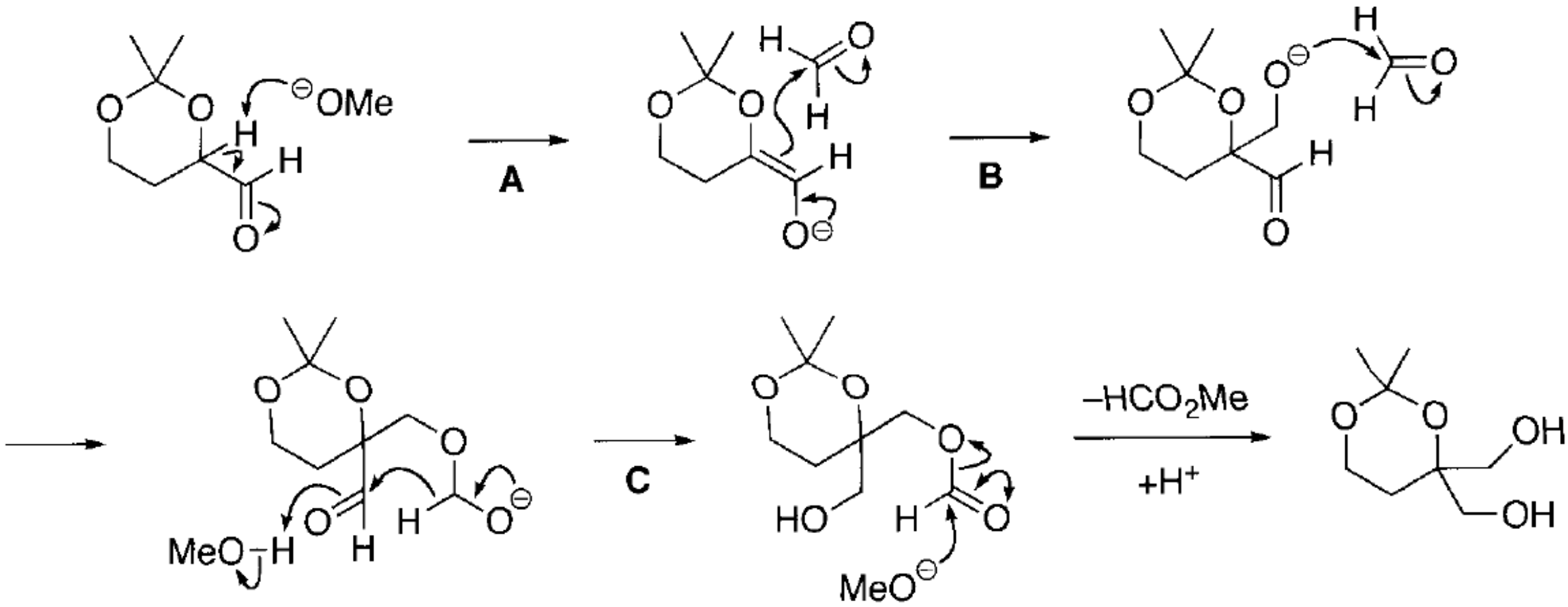
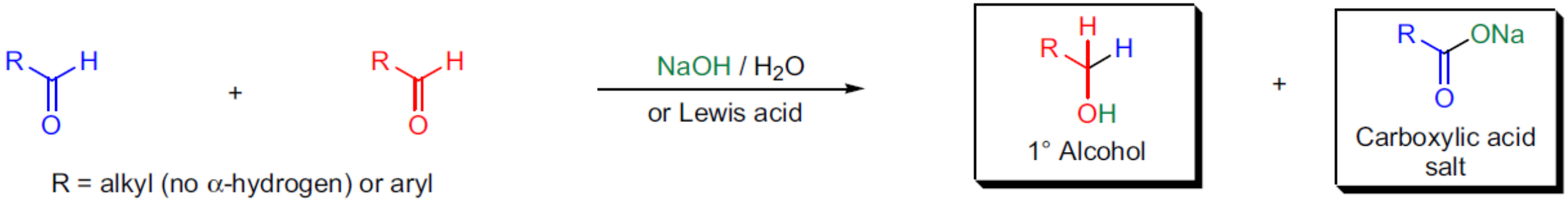
1.



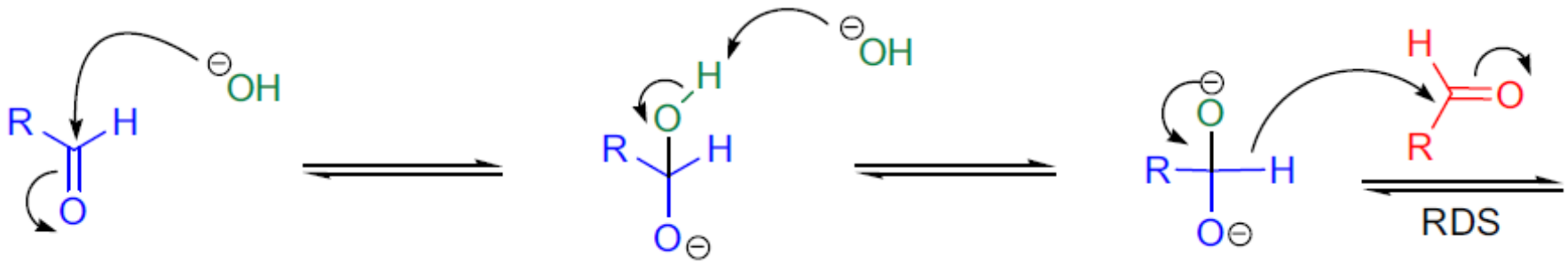


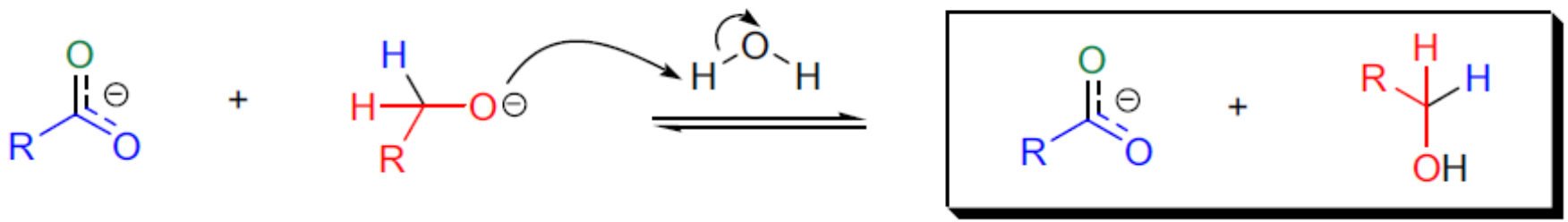
A: pKa MeOH = 15.5, CH_3CHO = 16.7. **B**: Aldol reaction. **C**: Intramolecular hydride transfer (Cannizzaro-type reaction).

Cannizzaro Reaction （P74）



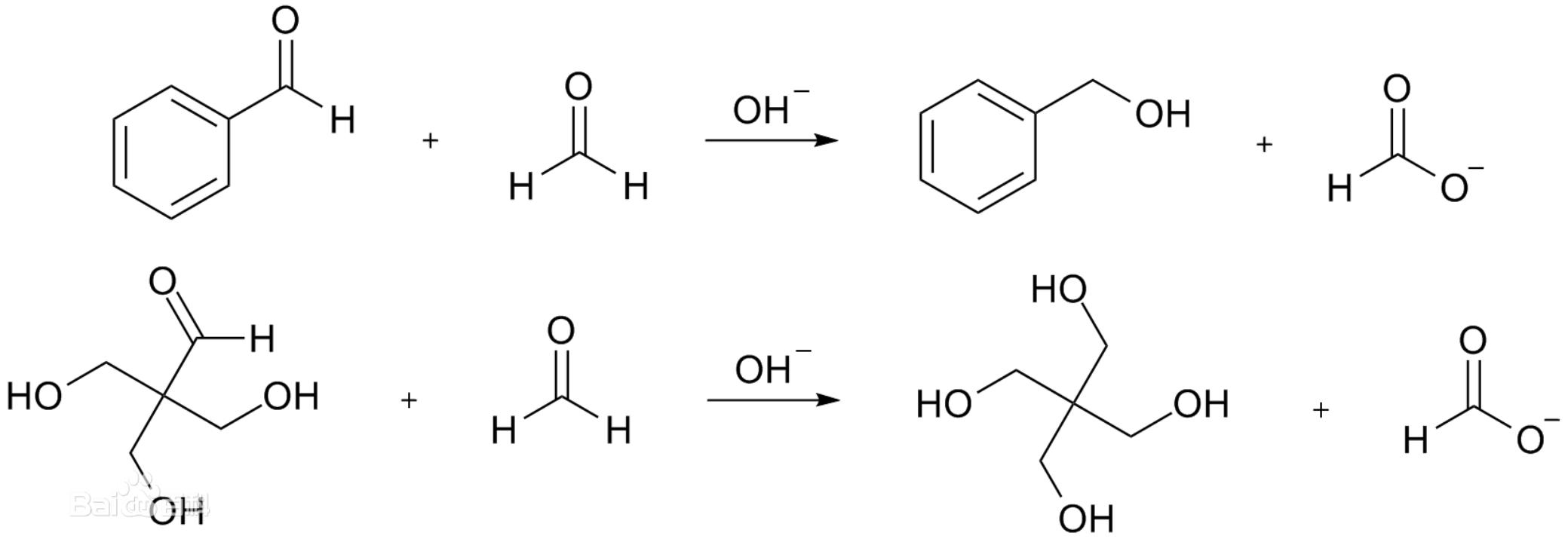
R = alkyl (no α-hydrogen) or aryl



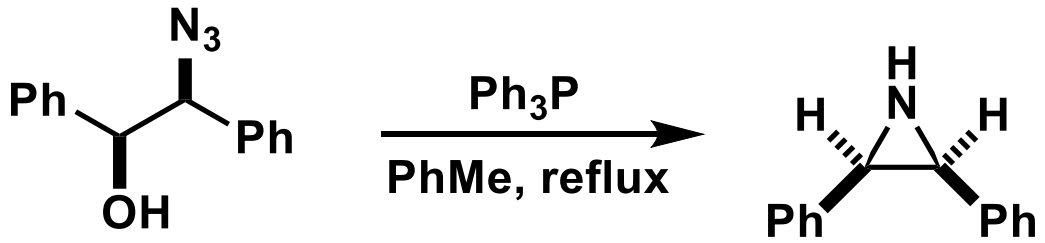


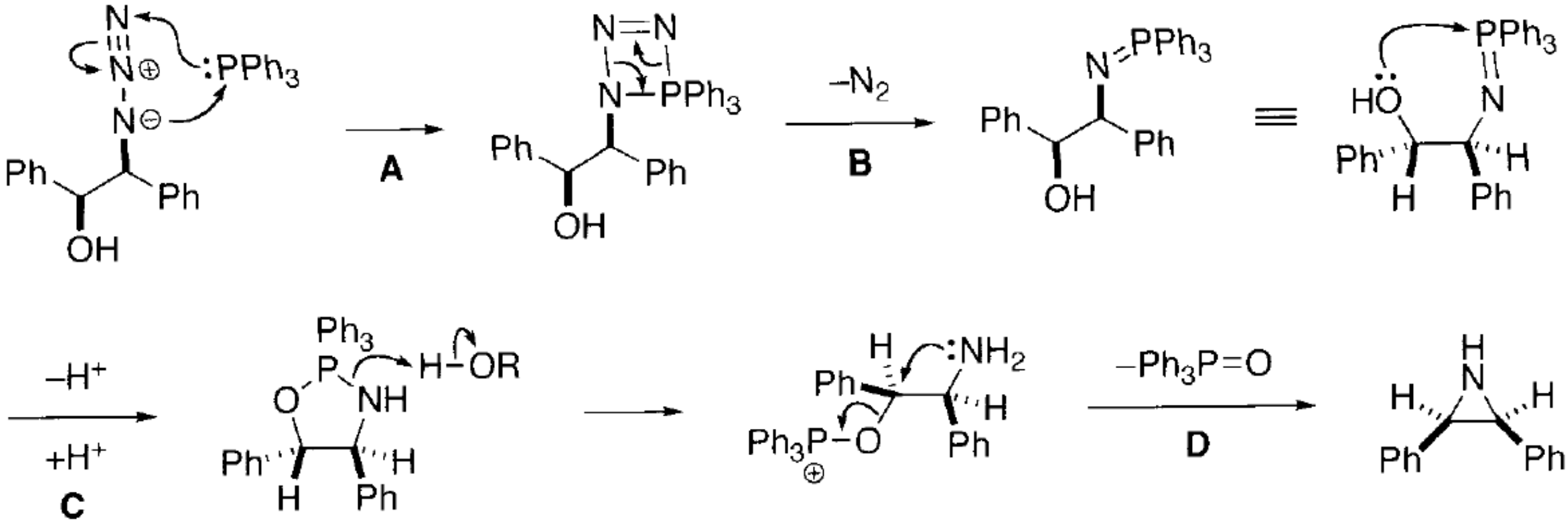
Crossed Cannizzaro Reaction

混合两个不同的不含α氢的醛，如甲醛和苯甲醛，使其在碱性条件下发生交叉氧化还原反应，称为交叉坎尼扎罗反应。由于甲醛在醛类中的还原性最强，因此总是自身被氧化为甲酸，而另一个反应物被还原为醇。工业上制取季戊四醇就是用的这个方法。



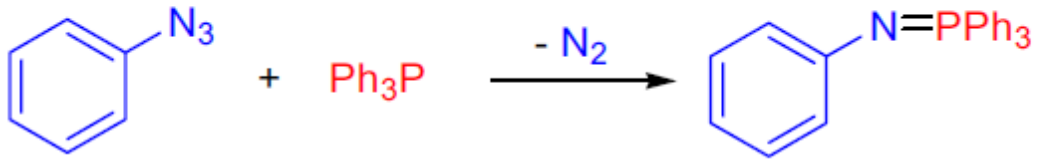
2.



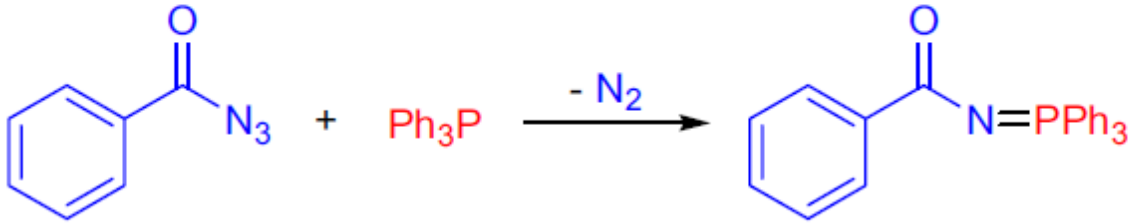

A
B
C
D
–N2
–H+
+H+
–Ph3P=O

Staudinger Reaction （P428）

Staudinger (1919):

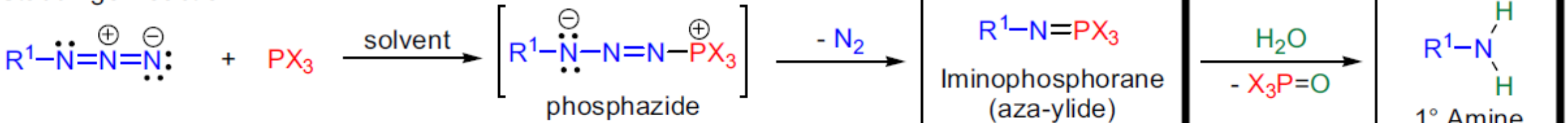


phenyl azide

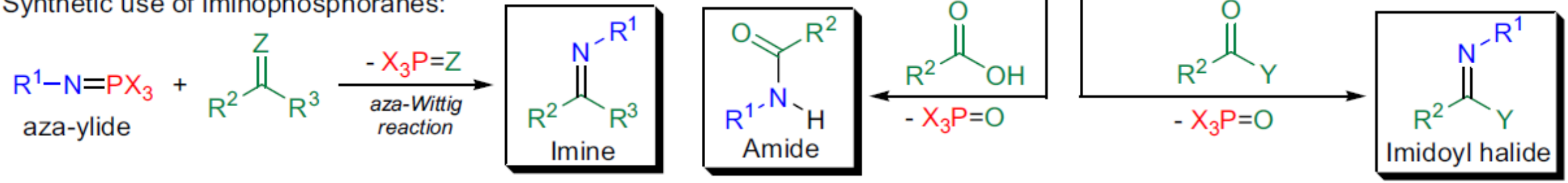


benzoyl azide

Staudinger reaction:

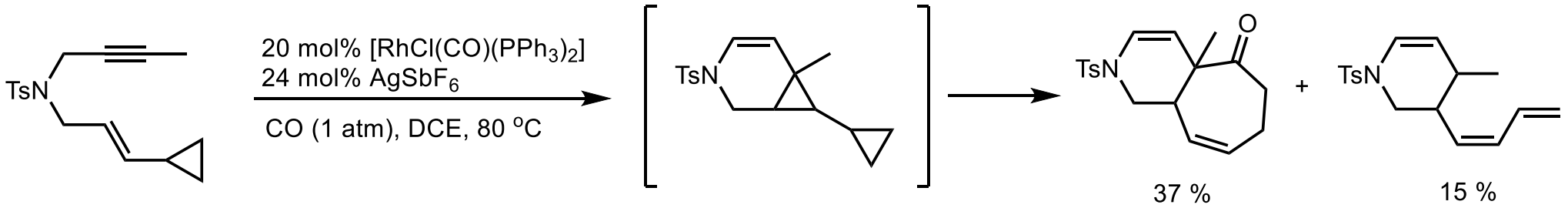


Synthetic use of iminophosphoranes:



R^1 = alkyl, aryl, heteroaryl, RC(O), RSO_2, RP(O), R_2P, R_3Si, R_3Sn, R_3Ge; R^{2-3} = H, alkyl, aryl, heteroaryl; X = alkyl, aryl, O-alkyl, O-aryl, NH_2, NR_2, Cl, F, NCO, (also the combination of these ligands); Y = Cl, Br; Z = O, S; solvent: THF, Et_2O

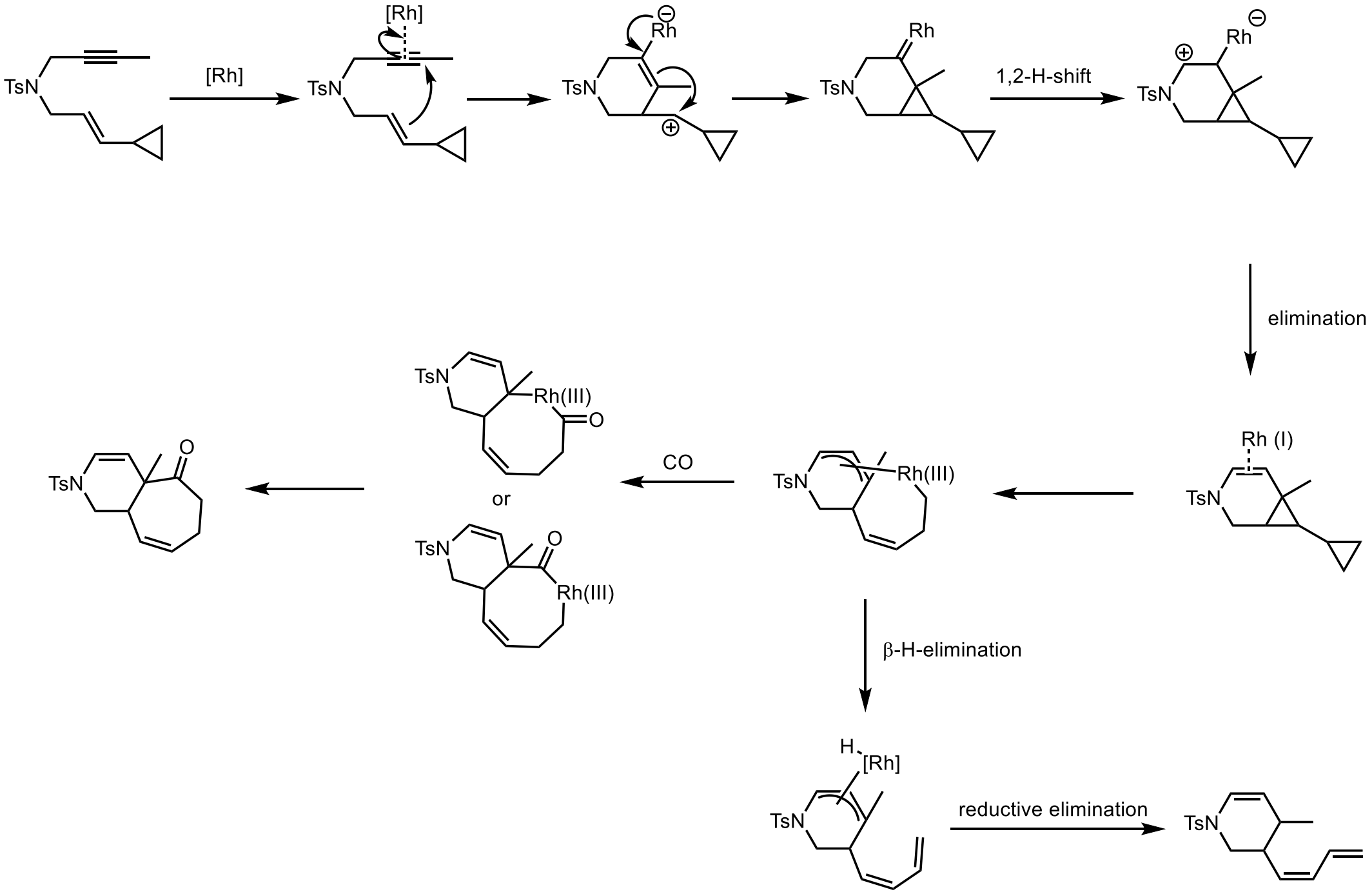
3.



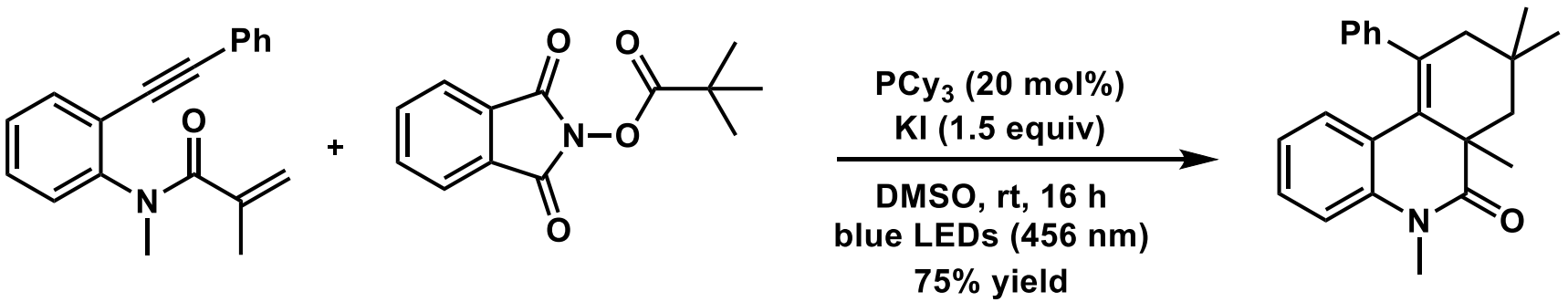
37 %

15 %

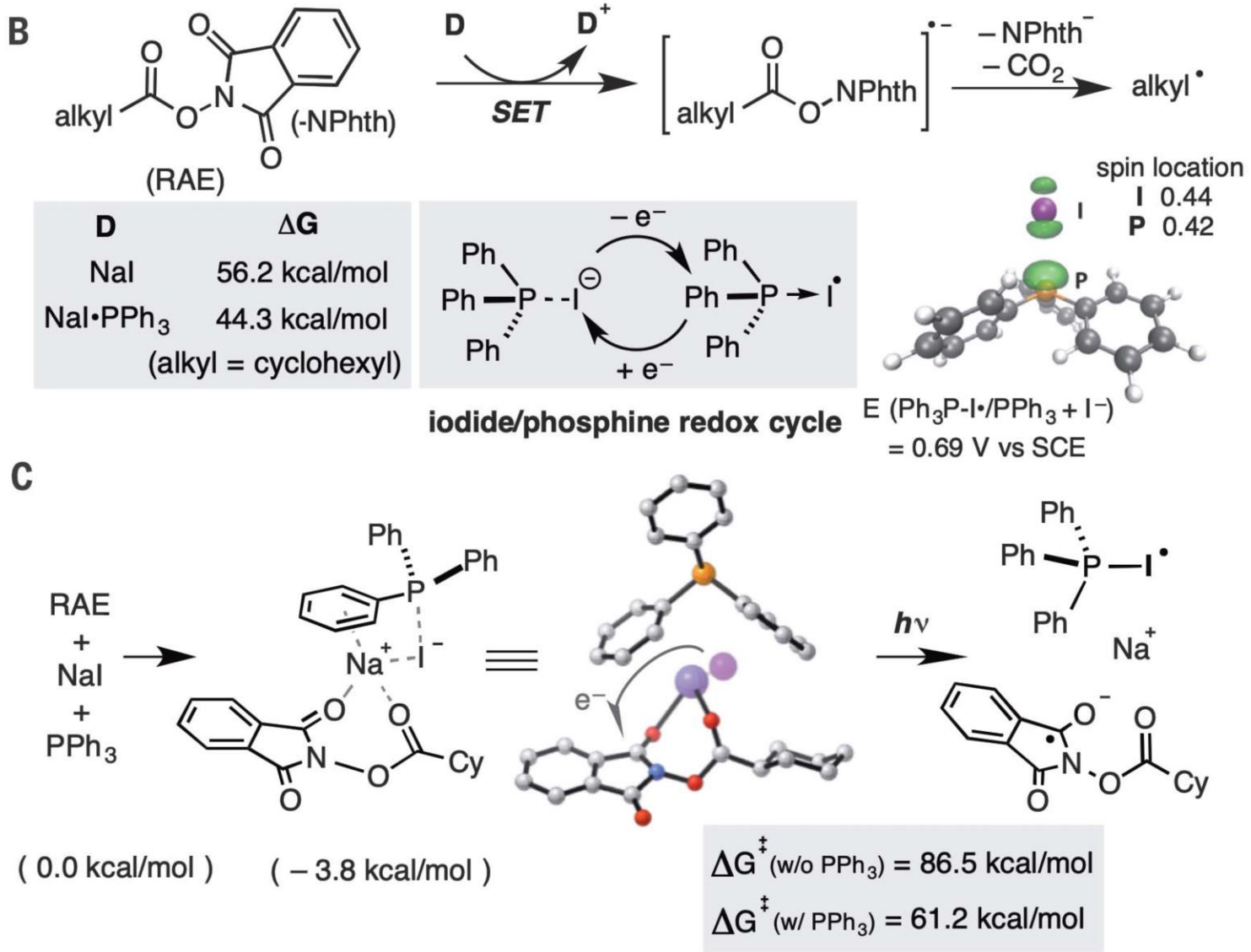
J. Org. Chem. **2010,** 75, 1281-1284


TsN
[Rh]
Rh
1,2-H-shift
elimination
Rh (I)
Rh(III)
CO
or
O
β-H-elimination
H
reductive elimination

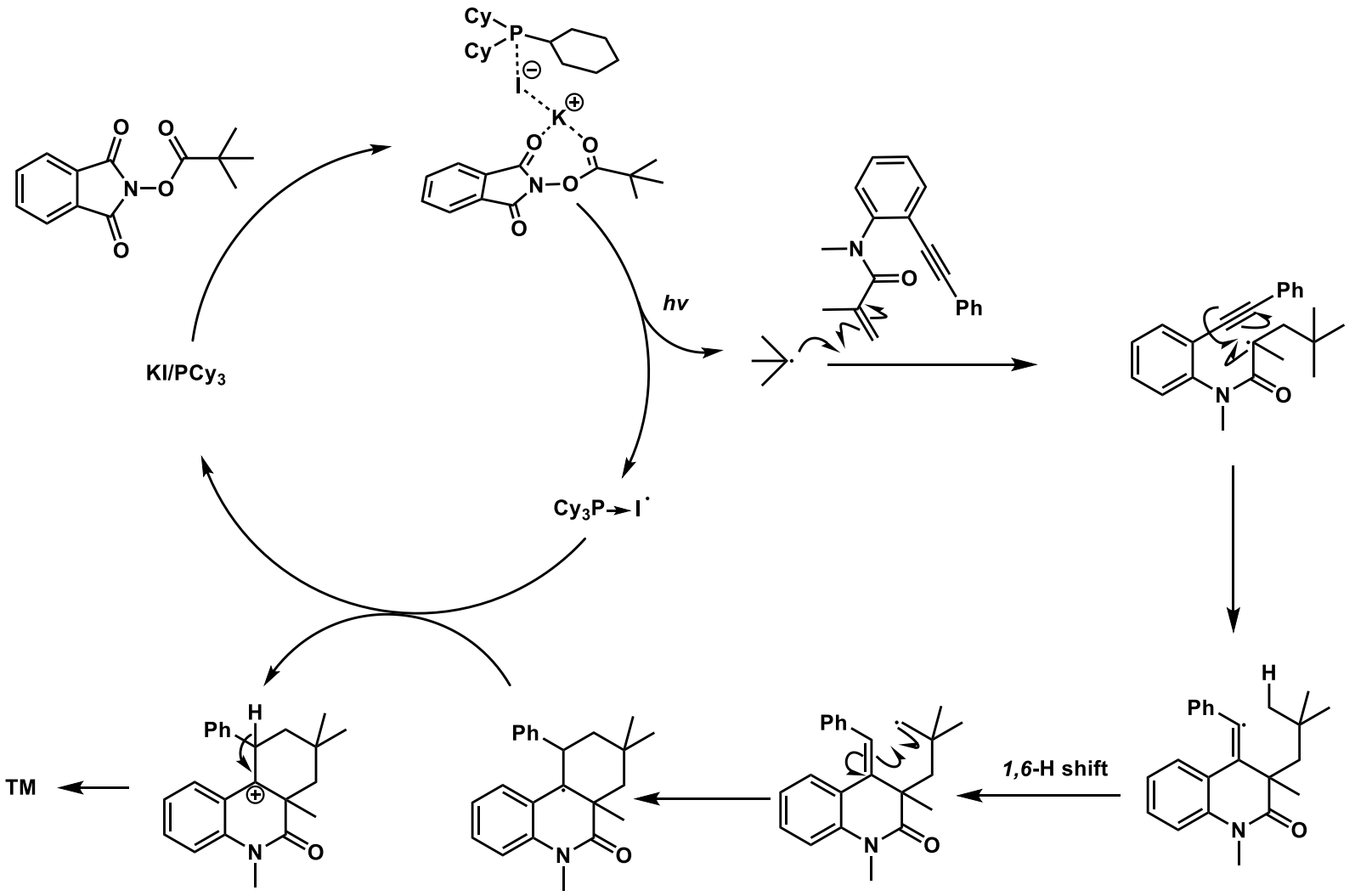
4.



DOI : 10.1021/acs.orglett.0c031821.



Science, **2019**, *363*, 1429–1434.


KI/PCy3
hv
Cy3P→I·
1,6-H shift
TM