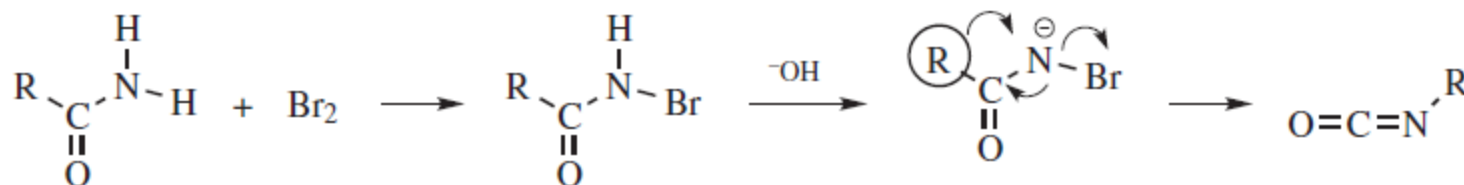
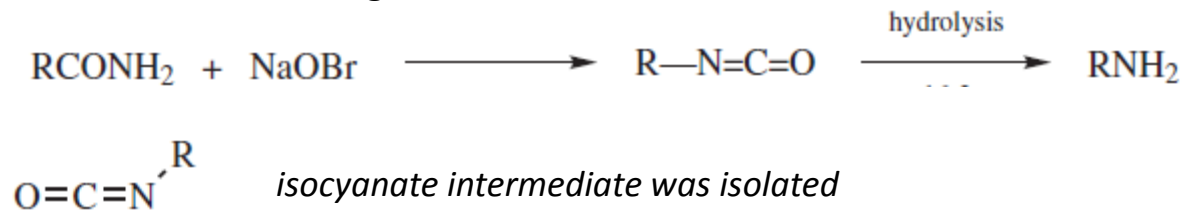


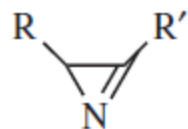
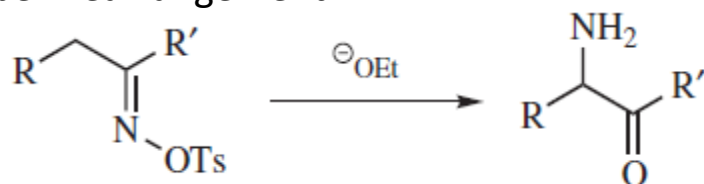
# 3. Study of Intermediates

## (i) Isolation of Intermediates

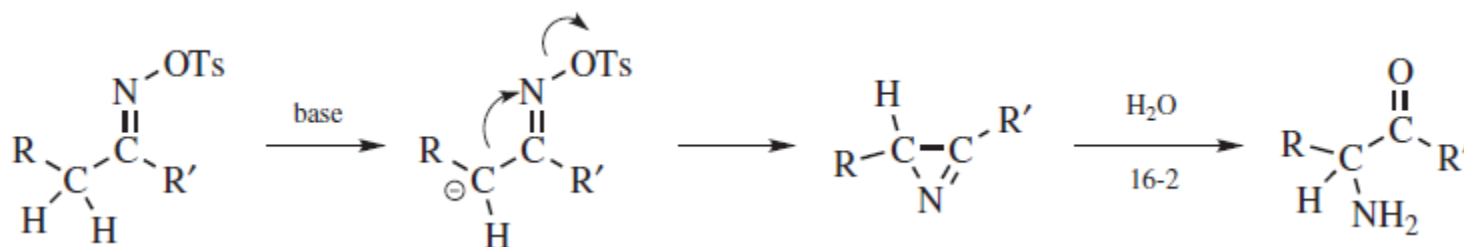
### Example-1: Hoffmann Rearrangement



### Example-2: Nebber Rearrangement

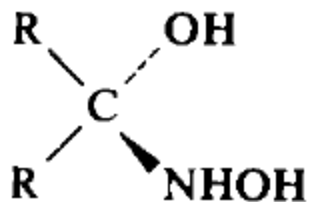
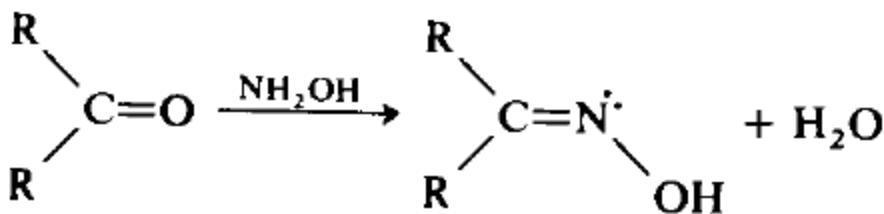


*an azirene intermediate was isolated*



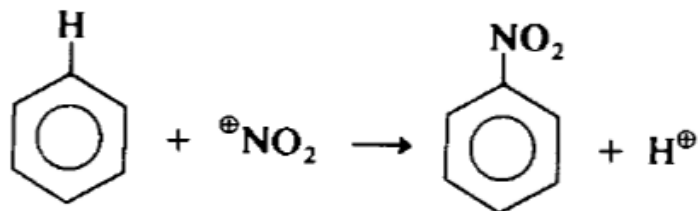
## (ii) Detection of Intermediates

Example-1



*Carbinolamine intermediate was detected by IR spectroscopy*

Example-2

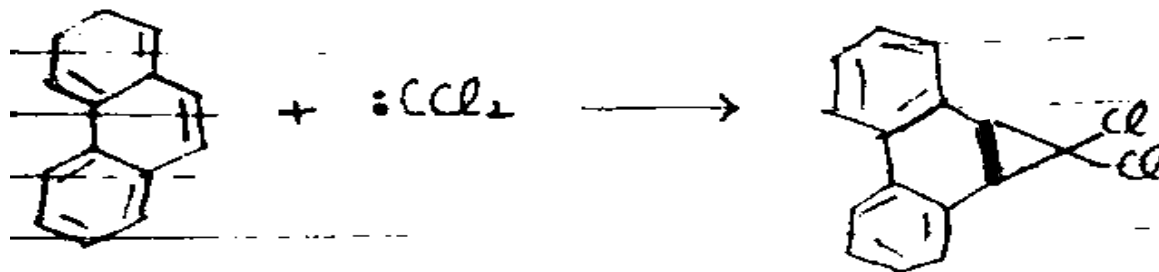
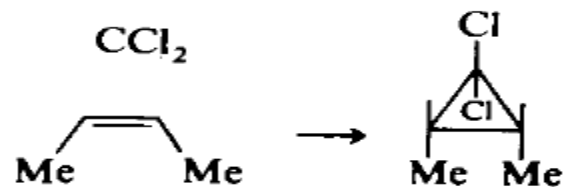


$\text{}^{\oplus}\text{NO}_2$  *Nitronium ion intermediate was detected by Raman Spectroscopy spectroscopy*

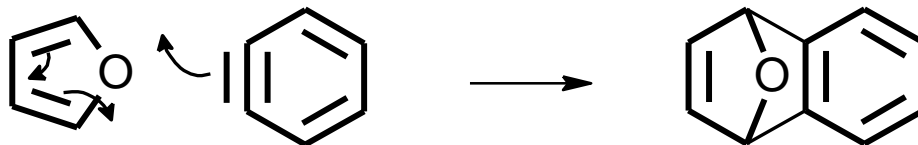
Example-3: Free radicals are detected by ESR spectroscopy

### (iii) Trapping of Intermediates

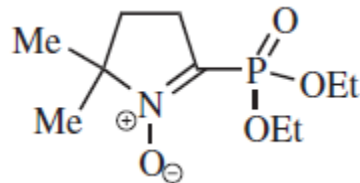
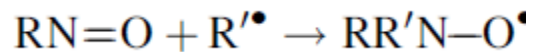
#### Example-1: Carbene Trapping



#### Example-2: Aryne Trapping

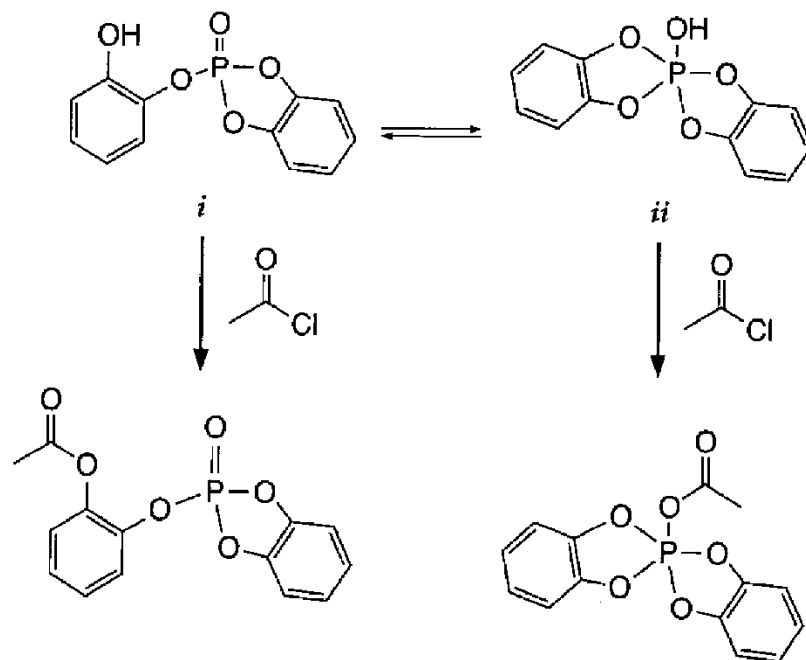


#### Example-3: Spin Trapping



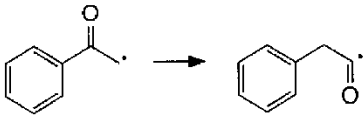
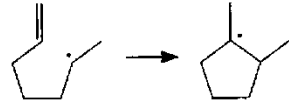
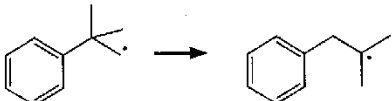
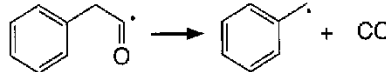
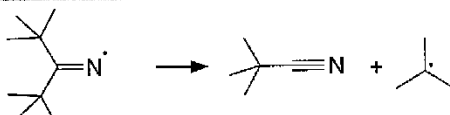
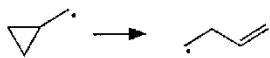
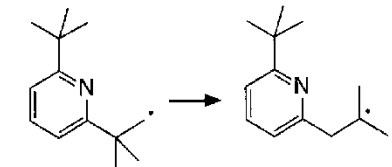

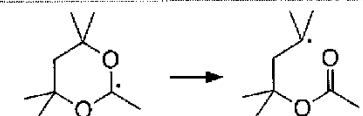
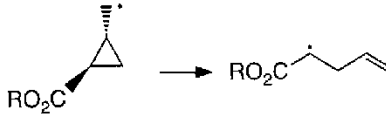

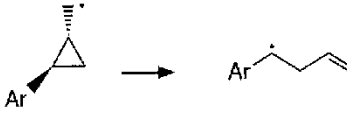
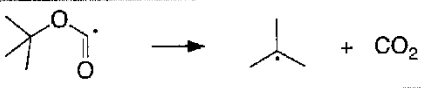
2-(Diethylphosphino)-5,5-dimethyl-1-pyrroline-N-oxide  
(Spin Trap)

# Trapping a Phosphorane Legitimizes Its Existence



# Techniques to Study Radicals: Clocks and Traps

Various Radical Clocks and Their Rate Constants for Rearrangements\*

Clock	Rate constant for rearrangement (s <sup>-1</sup> ), 25 °C	Clock	Rate constant for rearrangement (s <sup>-1</sup> ), 25 °C
	10		$1.3 \times 10^5$
	59		$5.2 \times 10^7$
	71		$1.3 \times 10^8$
	$7.8 \times 10^2$		$2 \times 10^9$
	$1.3 \times 10^3$		$(5-8) \times 10^{10}$
	$9.8 \times 10^3$		$(1-4) \times 10^{11}$
	$3.3 \times 10^4$		

\*Griller, D., and Ingold, K. U. "Free Radical Clocks." *Acc. Chem. Res.*, **13**, 317 (1980). Newkomb, M., and Toy, P. H. "Hypersensitive Radical Probes and the Mechanisms of Cytochrome P450-Catalyzed Hydroxylation Reactions." *Acc. Chem. Res.*, **33**, 449 (2000).