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TUNGHAI UNIVERSITY

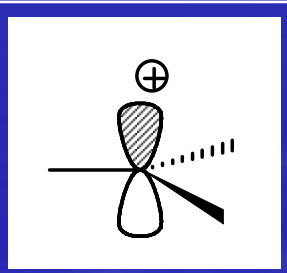
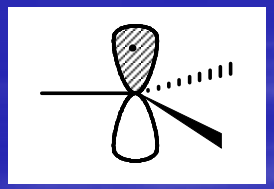
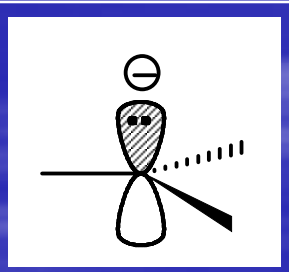
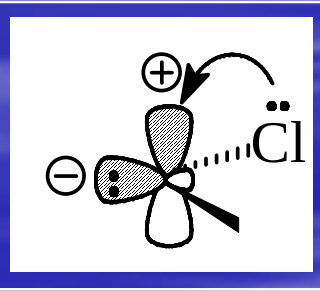
有機化學實驗

Dichlorocarbene

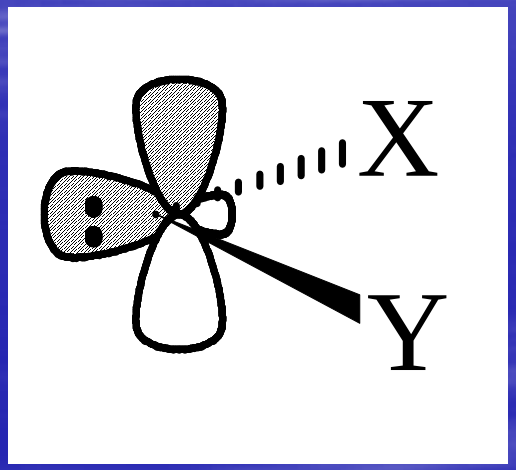
相轉移催化和碳烯反應
二氯碳烯和環己烯的反應

原　理

1. Some intermediates of carbon:

Names	Carbocation	Carbon radical	Carbanion	Carbene
Structures				
Others	Electrophilic	Electrophilic	Nucleophilic	Electrophilic

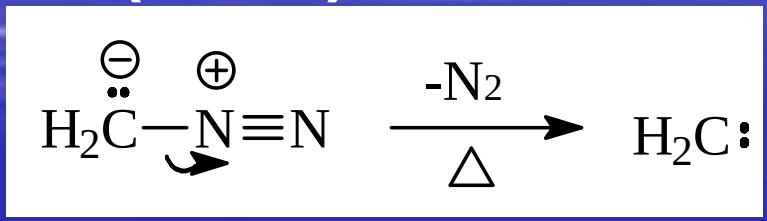
2. Stability of carbene:



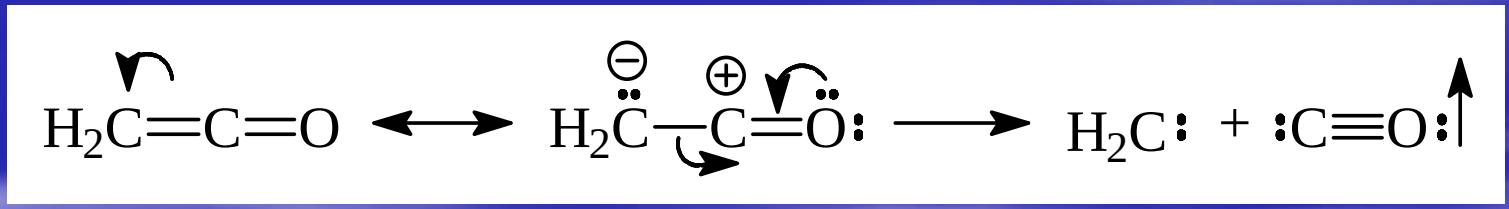
X,Y=halide,OH > X=halide,OH;Y=H > X,Y=H

3. Preparation of carbene :

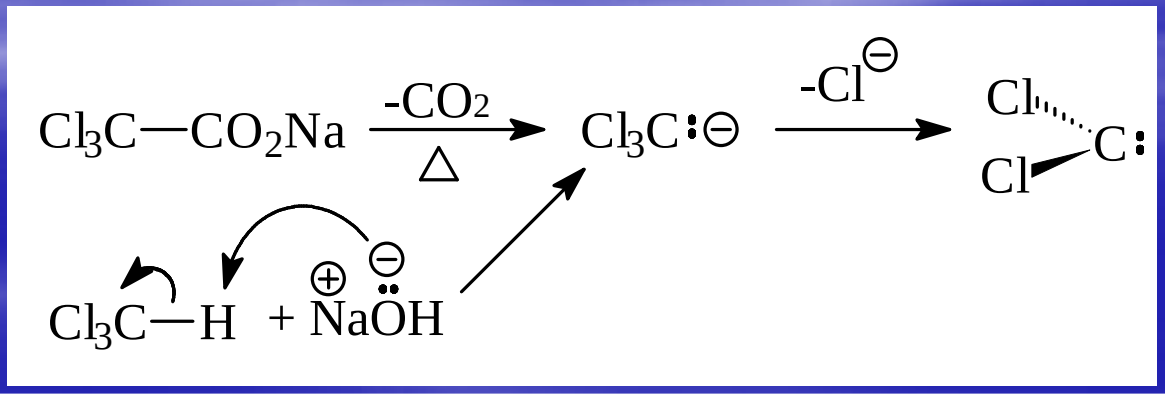
(1) Diazomethane (CH_2N_2):



(2) Ketene ($H_2C=C=O$):

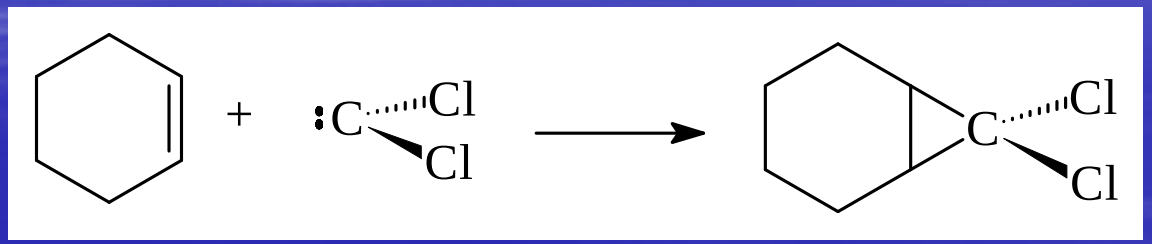


(3) Preparations of dichlorocarbene:

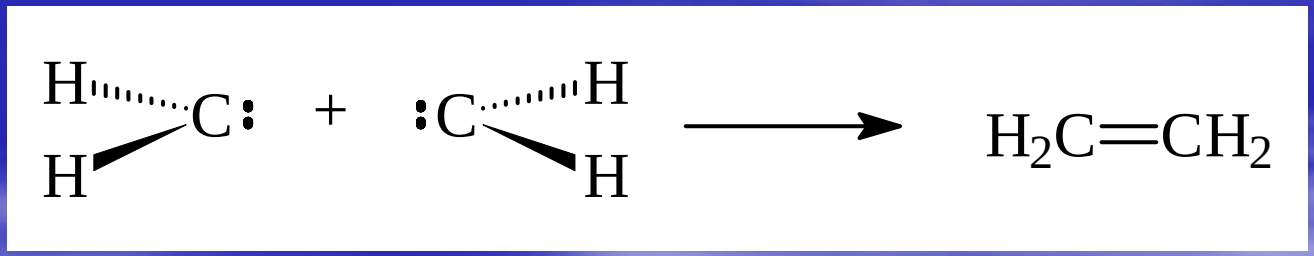


4. Reaction of carbene:

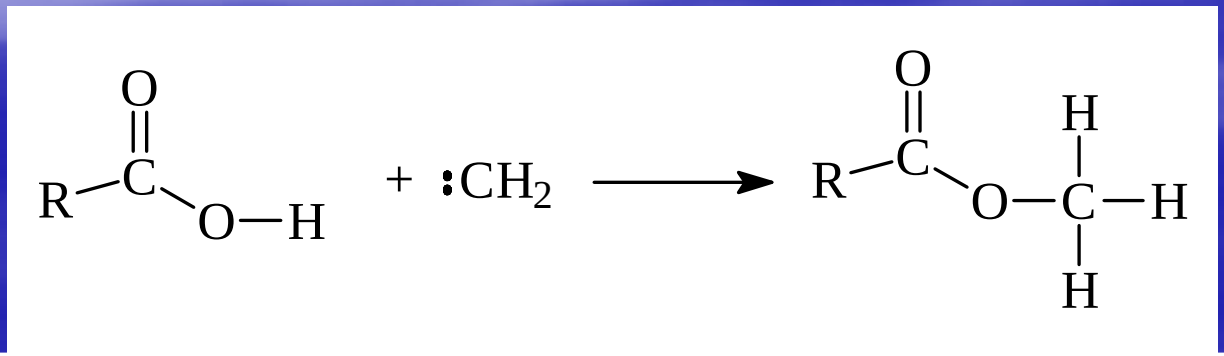
(1) Electrophilic cyclopropanation:



(2) Dimerization:



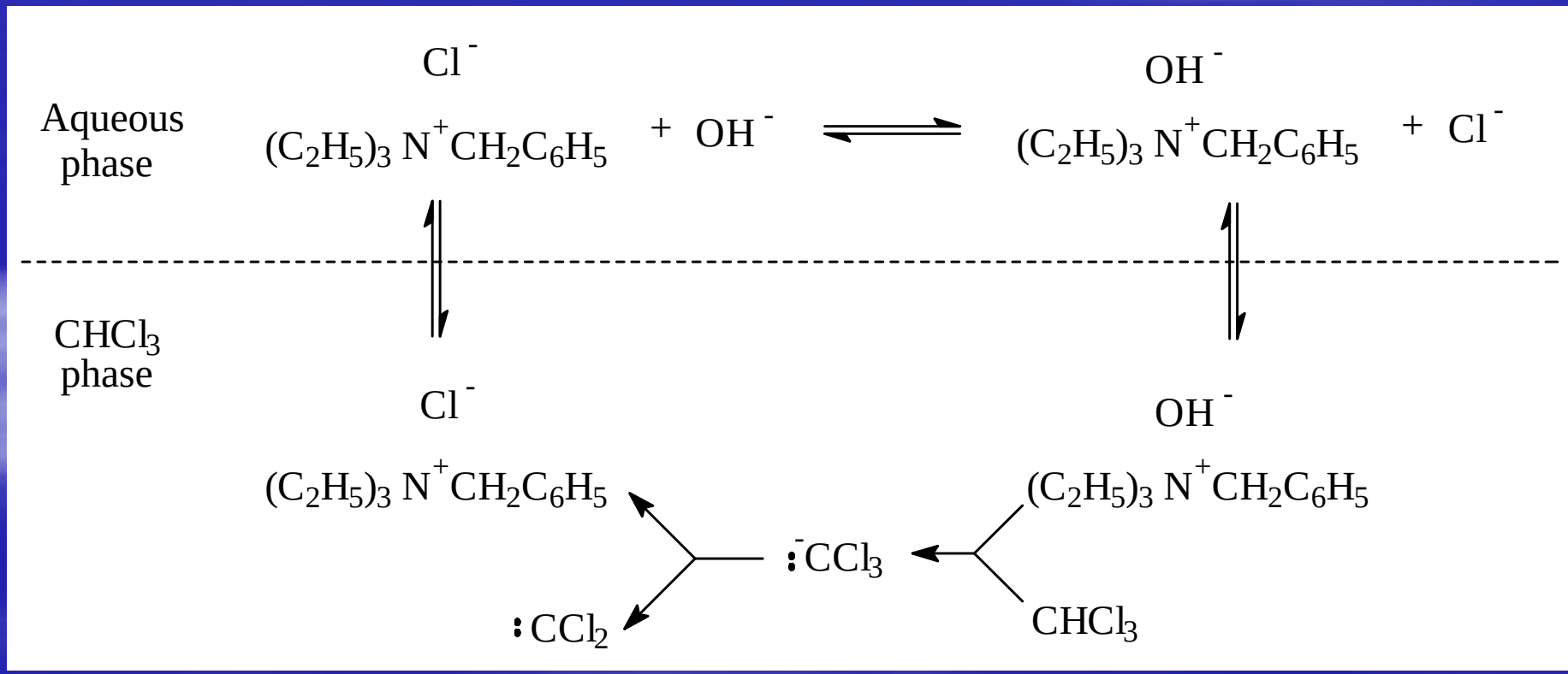
(3) Insertion:



5. Phase transfer catalyst: (crown ether, benzyltriethylammonium chloride,…)

(1) Aqueous phase: H_2O, Na^+, HO^-, benzyltriethylammonium chloride

(2) $CHCl_3$ phase : cyclohexene, $CHCl_3$, benzyltriethylammonium chloride



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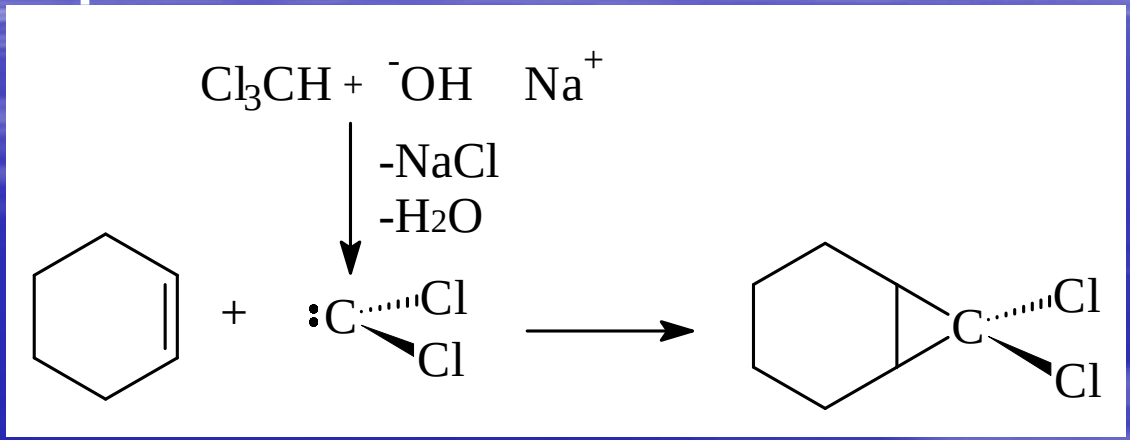
Reaction equation:



4.1g(5.05mL) cyclohexene + 4.2mL $CHCl_3$ +
10mL 50% NaOH in 50mL R.B. flask

↓(two phase)

add 0.2g benzyltriethylammonium chloride

↓(ice-water bath)

control the temp=50~60℃ for 10 min

↓

cool to 35℃ (形成土黃色乳化層)

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↓

dilute the mixture with 25mL dist. water

↓

separate the layers (separatory funnel)

↓(lower layer : $CHCl_3$)

extract the aqueous with 5 mL ether

↓

collect the ether layer and combine the organic layer

↓

wash with 10 mL H_2O

↓

collect the organic layer and dry with $MgSO_{4(anhy)}$

until the liquid is clean

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↓

distill to get the product b.p.=195~200℃
(b.p.≒100℃ at P=36mmHg)

↓

calculate the % yield (result report)

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Check out

1. 繳交產物並告知產物淨重。

2. 實驗問題：1 , 3