

SUBSTITUTION REACTIONS



SUBSTITUTION

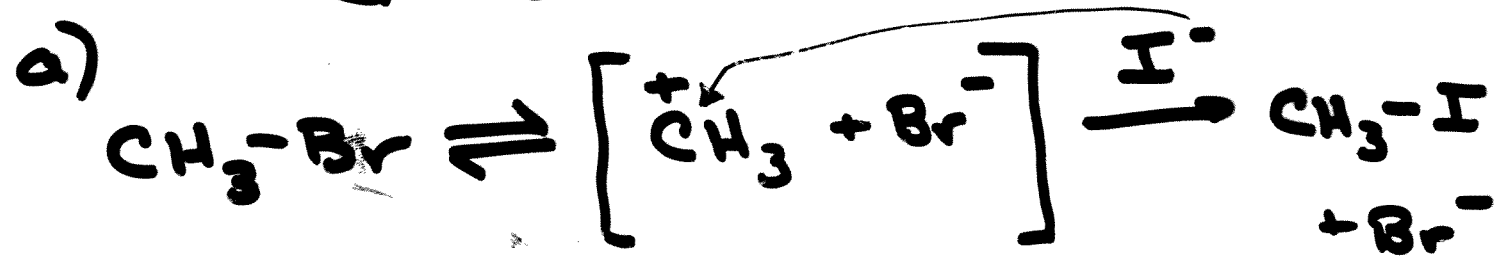
- REPLACING Br WITH I

How DOES THIS OCCUR?

TWO MAJOR, DOMINANT, LIMITING MECHANISMS.

1) S_N1 MECHANISM

- CARBOCATION ROUTE

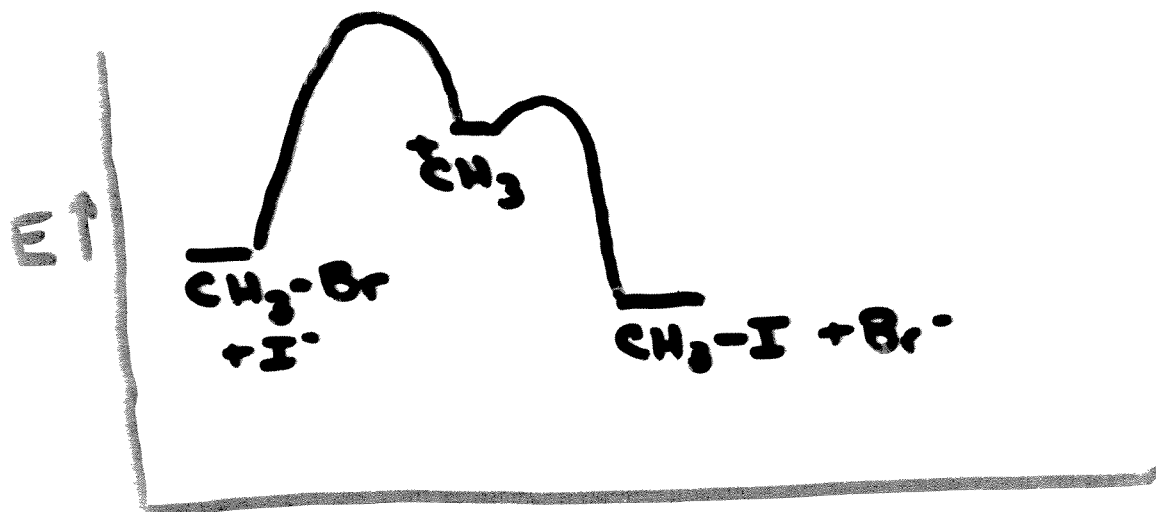


- HAS A CARBOCATION INTERMEDIATE

- TWO STEPS.

- TOUGH ONE - SEPARATING A NEUTRAL SPECIES INTO A PAIR AN ION PAIR.

- EASY ONE - RECOMBINING A PAIR OF IONS INTO A NEUTRAL CPD.



Rxn. Coord.

1st step is slowest

$$\text{Rate } v = k [\text{CH}_3\text{-Br}]$$

∴ 1st order.

S_N1

S - Substitution

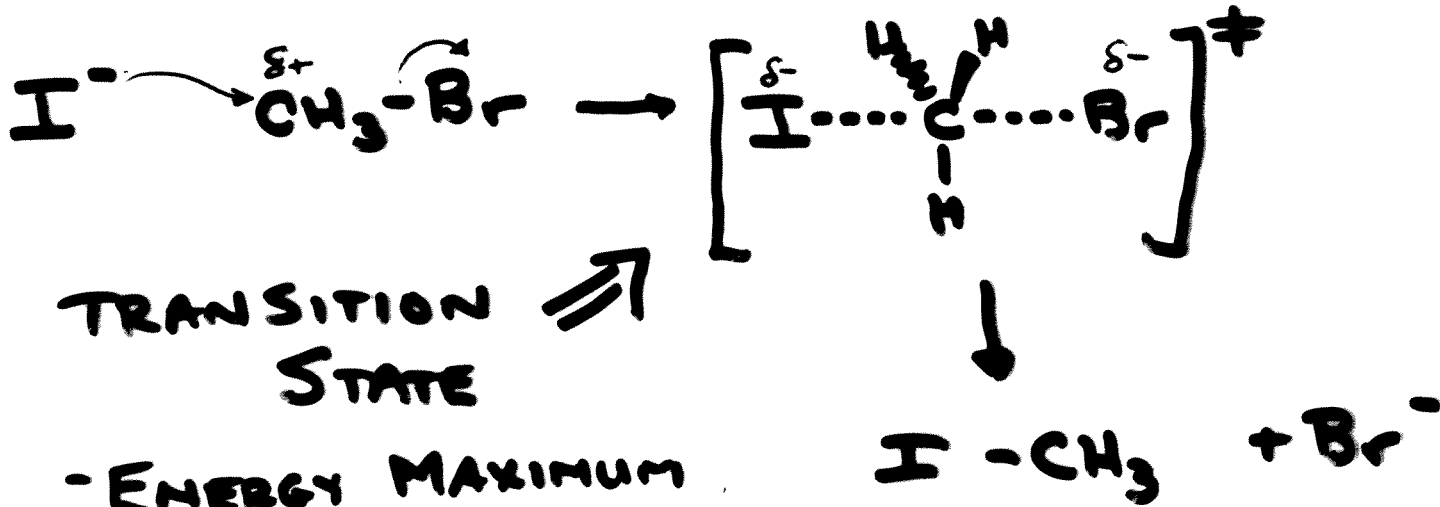
N - Nucleophilic

1 - 1st order

2) S_N2 Substitution.

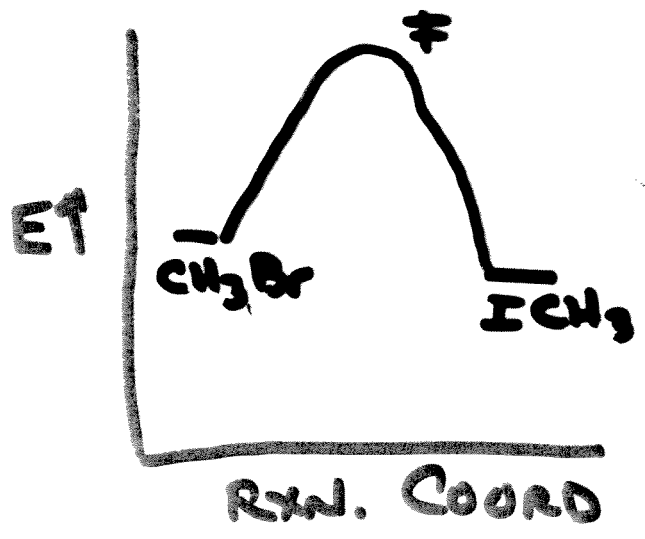
- Concerted.

- All bond making, bond breaking events occur at the same time



TRANSITION STATE

- ENERGY MAXIMUM
- NO LIFETIME
- ONLY ONE STEP.



- BOTH I^- AND CH_3-Br ARE CONSUMED IN SLOW STEP

RATE $v = k [CH_3Br] [I^-]$
 2ND ORDER OVERALL.

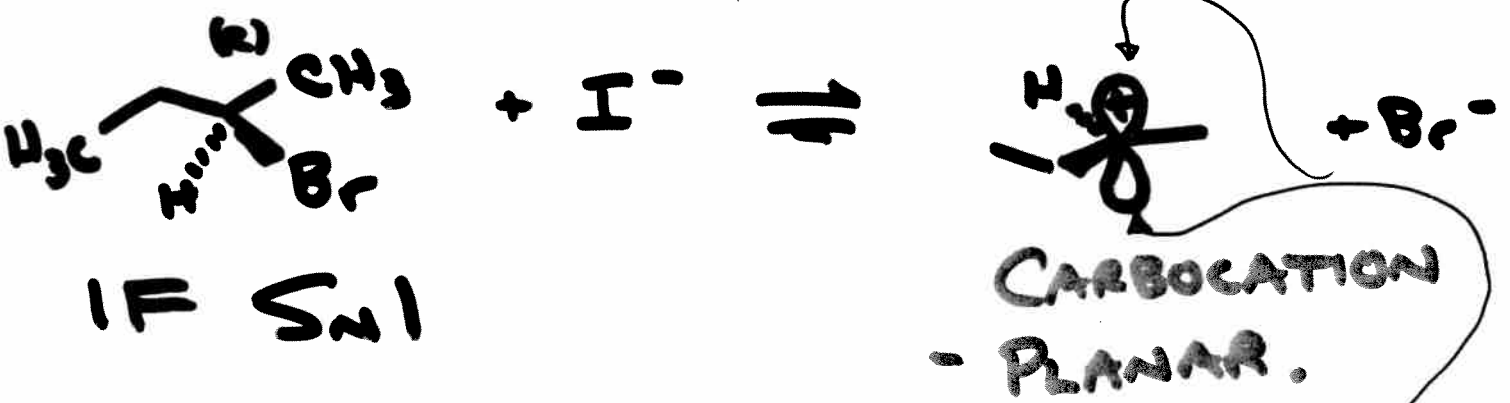
S_N2 S - SUBSTITUTION
 N - NUCLEOPHILIC
 2 - 2ND ORDER.

NOTE - THERE ARE CASES THAT ARE MOST ONE MECHANISM, BUT A BIT OF THE OTHER.

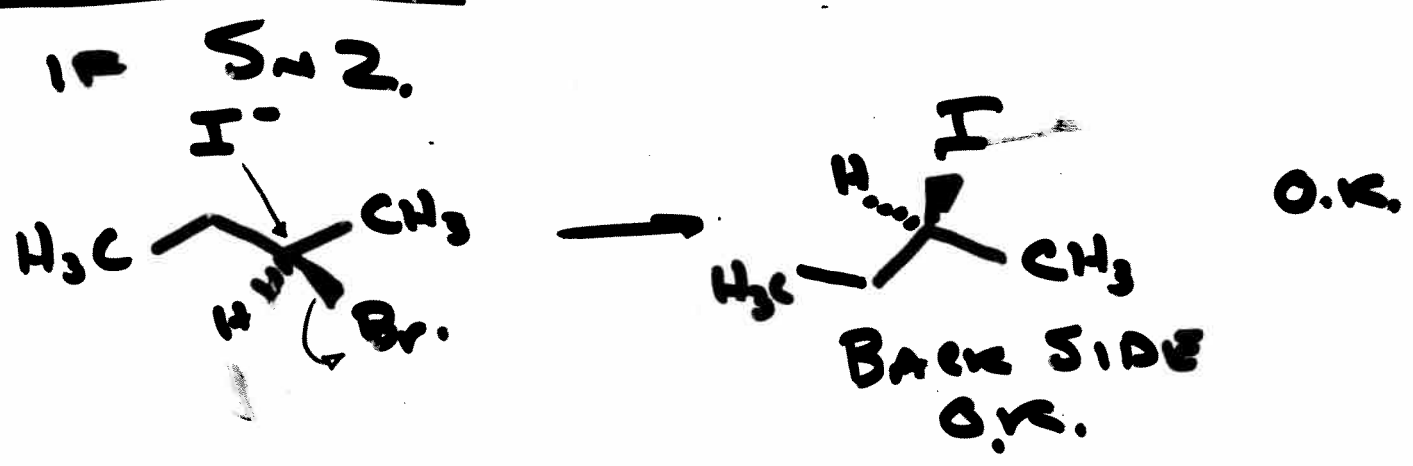
- THERE ARE A COUPLE OF MINOR ALTERNATIVE S_Ni

STEREOCHEMISTRY.

- WHAT HAPPENS FOR S_N1, S_N2.



∴ RACEMIC MIXTURE (50:50)
 LOSS OF STEREOCHEMICAL INFO.
 - RACEMIZATION.





SINCE FRONT IS BLOCKED, GET
100% INVERSION OF CONFIGURA-
TION AT CHIRAL CENTRE.

NOT ALWAYS (R) TO (S) - OR
(S) TO (R) - , BECAUSE INCOMING
GROUP MAY HAVE DIFFERENT
PRIORITY THAN LEAVING GROUP.