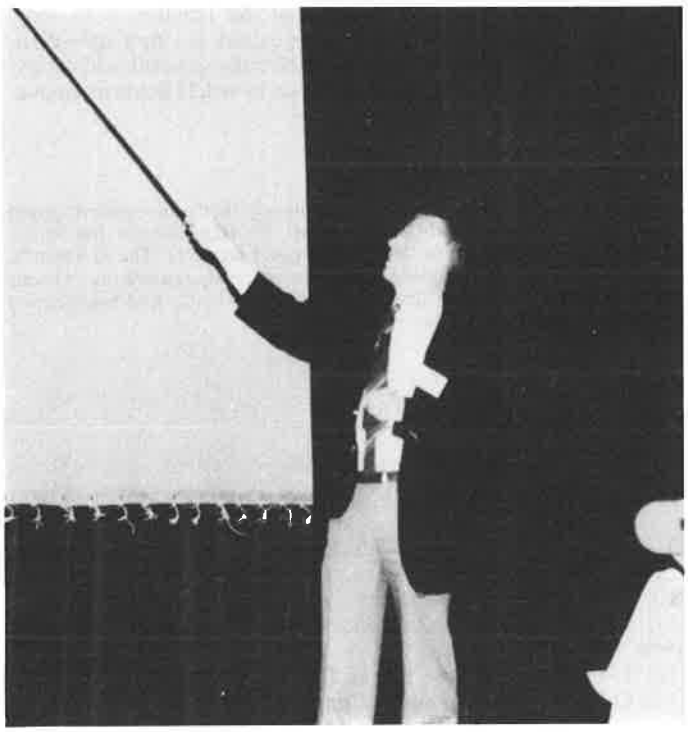
Thème "Fonctionnalisation des organobromés"

René Beugelmans

Halogens as leaving groups in radical nucleophilic substitution reactions ($S_{RN}1$)



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Dans sa conférence sur "Halogens as leaving groups in radical nucleophilic substitution reactions".

The $S_{RN}1$ mechanism for aliphatic or aromatic substitution on a substrate AX is initiated by monoelectronic transfer leading to the radical anion $AX^{\bullet -}$ (1). This unstable odd electron species extrudes X^- to give the radical $A^\bullet$ (2). This latter electrophilic intermediate, attacked by the nucleophile gives a radical anion $ANu^{\bullet -}$, (3), precursor of the final product. In the last step (4), $ANu^{\bullet -}$ is oxydised by AX to give the substitution product ANu and $AX^{\bullet -}$, the formation of which sustains the chain process.

$$\boxed{AX} \xrightarrow{e^-} AX^{\bullet -} \qquad (1)$$

$$AX^{\bullet -} \longrightarrow \boxed{X^-} + A^\bullet \qquad (2)$$

$$A^\bullet + \boxed{Nu^-} \longrightarrow ANu^{\bullet -} \qquad (3)$$

$$ANu^{\bullet -} + AX \longrightarrow \boxed{ANu} + AX^{\bullet -} \qquad (4)$$

The role of the halides as leaving groups for $S_{RN}1$ chemistry - with emphasis on Br^- - will be illustrated by selected examples of aliphatic and aromatic reactions.

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