QUATERNARY AMINO CLAISEN REARRANGEMENT

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Generalities of quaternary amino Claisen rearrangement of aromatic quaternary ammonium salts were investigated as a typical mode of charge induced Claisen rearrangement.

N-Allylanilinium salts whose ortho positions were open, e.g., N-allyl-N,N-dimethylanilinium halides, N-allyl-N,N-dimethyl-p-anisidinium bromide and N-allyl-N,N,-dimethyl-p-hydroxyanilinium bromide, rearranged to give corresponding ortho allylaniline derivatives in good yields.

Ortho substituted salts such as N-allyl-N,N-dimethyl-o-toluidinium halides and N-allyl-N,N-dimethyl-o-anisidinium salts gave poor to trace amount of ortho rearrangement products. On the other hand 1-allyl-1-methyl-1,2,3,4-tetrahydroquinolinium salts as mono ortho substituted salt rearranged into 8-allyl-1-methyltetrahydroquinolines in good yields.

As a substrate whose two ortho positions were occupied 4-allylated-julolidinium halides were subjected to rearrangement. 4-Allyl- and 4-crotyl-julolidinium halides yielded 9-allyl- and 9-crotyl-julolidine respectively.

When 9-substituted-4-allylated-julolidinium salts were exposed to the rearrangement as a substrate whose all ortho and para positions were preoccupied allyl group moved to meta position. These could be the first observation of meta rearrangement in amino Claisen rearrangement.

Mechanistic investigations suggest that these quaternary amino Claisen rearrangement are intramolecular [3,3] sigmatropic rearragement. Meta rearrangement of allyl group could be explained by the combination of [3,3] and [1,2] sigmatropic rearrangements. Plausible mechanism was proposed.