THE REACTIONS OF ASYMMETRIC TERTIARY AMINES WITH ELECTROPHILIC REAGENTS

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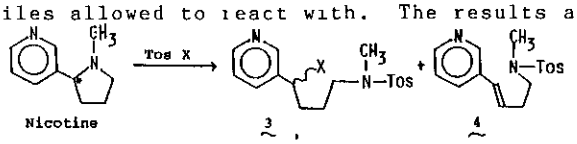
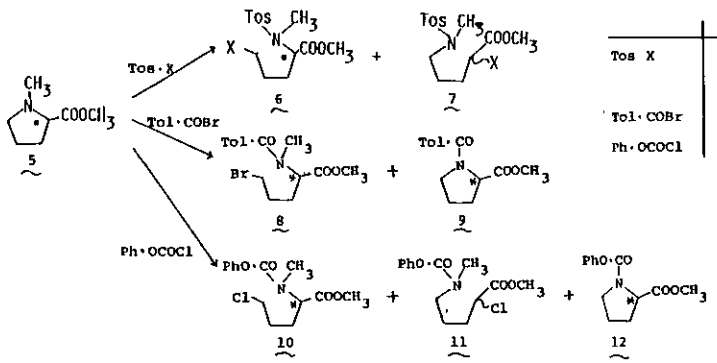
The title reactions are investigated and preferential C-N cleavage of the amines and their reactivity depending on the chemical structures of the amines and the electrophiles are discussed. 2-Benzylquinuclidine reacts with p-tosyl chloride 1 to give the two different sulfonamides, 4-(1-phenylallyl)-1-tosyl-piperidine and 2-benzyl-4-(2-chloroethyl)-1-tosylpiperidine, while with p-tosyl bromide 2 to give only 2-benzyl-4-(2-bromoethyl)-1-tosylpiperidine. Nicotine reacts with 1 and 2 give exclusively the products, 3a-b and 4, resulted from the bond scission between the 2-pyridyl-substituted carbon and the nitrogen atoms. This is interpreted in terms of S_N1 type reaction due to the highly preferential development of carbonium ion character of the carbon atom. N-methylproline methyl ester 5 shows multiplicity in the reaction behaviors depending on the electrophiles allowed to react with. The results are summarized below.





	Products (Yield %)					
Tos X	6a (10)	7a (14)				
	6b (18)	7b (27)				
Tol·COBr	8 (31)	9 (10)				
Ph·OCOCl	10 (64)	11 (14)	12 (12)			

X = a)Cl, b)Br

Tol =