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STUDIES ON HETEROCYCLIC QUATERNARY NITROGEN BASES : KINETICS OF TRANSALKYLATION OF PRIMARY AMINES BY N-SUBSTITUTED 5,6-DIHYDRO-2,4-DIPHENYLNAPHTHO[1,2-b]PYRIDINIUM CATIONS

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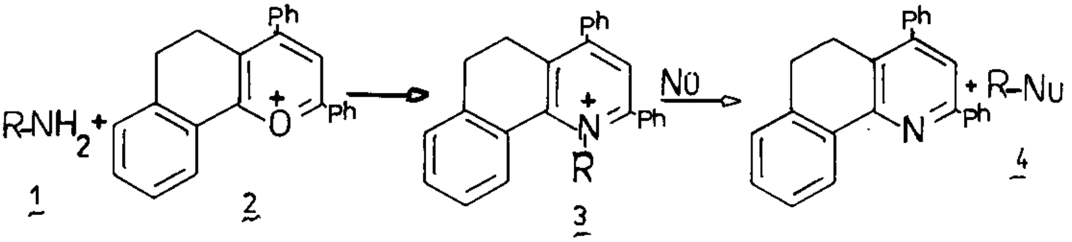
__Abstract__- N-substituents in 5,6-dihydro-2,4-diphenylnaphtho-[1,2-b]pyridiniums are transferred to piperidine by unimolecular and / or bimolecular processes in chlorobenzene solution. The Kinetics of this reaction at variable temperatures were studied. It has been shown that the reaction follows either S_N1 or S_N2 mechanisms dependant on the nature of N-substituent.

The displacement of N-alkyl, N-heteroaryl and N-benzyl substituents from 2,4-diphenyl-5,6-dihydronaphtho[1,2-b] pyridinium tetrafluoroborate 3 by piperidine as a nucleophile converts primary amines 1 into a wide variety of functionalities 4 . These reactions are of considrable synthetic potential and have already led to several novel transformations[1,2]. Previous studies[3] indicated that N-substituents could be transplanted from 2,4,6-triphenylpyridiniums by S_N1 or S_N2 mechanisms.



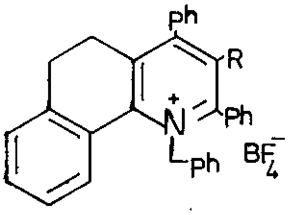
To attain such reactions under mild conditions, we studied the effect of C-3 substituents in the pyridinium ring on the kinetic rates for transfer of N-substiuents to piperidine. Spectrophotometric method used was for determining the rate constants of the reaction. The kinetic runs were carried out in chlorobenzene at temperature range 40-100°C and samples were quenched by ice cooling, then measuring the absorbance at 345 nm. N-Alkyl, benzyl and heteroarylpiperidines thus produced were confirmed by synthetic methods[4]. In all cases, the observed rate was a linear function of the piperidine concentration. The rate variations could be interpreted in terms of either S_N2 reaction or a combination of S_N1 and S_N2 mechanisms, values of k_1,k_2 and activation parameters are given in Table 1. N-Benzyl compounds are displaced essentially completely via the S_N2 mechanism[3]. Replacement of the 3-H in compound 5 by a 3-phenyl (6), 3-methyl (7) or 3-ethyl (8) reduces the S_N2 rate constants (k_2) by factor of ca. 20, 10 and 9,respectively, because of butterssing effect. Consideration of the previous pattern of compounds demonstrates that S_N2 rates do not simply increase by introduction of different substituents in C-3 because of the existance of S_N1 mechanism which lowers the S_N2 rate for compounds 6, 7, and 8. The reactions of a series of N-substituted 2,4-diphenyl-5,6-dihydronaphtho[1,2-b]pyridiniums with piperidine clearly proceed almost entirely by a second order process for methyl, ethyl, allyl and benzyl. but the reaction proceeds by both first order and second order for 2- and 4-pyridyl.

Table 1. First and second order rate constants at 100°C in chlorobenzene solution.

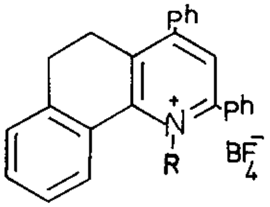
Cpd. No.	C-substituents 2	3	4	N-substituents	$k_1.10^5$ sec^{-1}	$k_2.10^3$ $l\ mol^{-1}$ sec^{-1}	E_A $kcal.mol^{-1}$	H_{373} $kcal.mol^{-1}$ deg^{-1}	S_{373} $kcal.mol^{-1}$ deg^{-1}
5	Ph	H	Ph	benzyl	36.66	226.34	15.80±2.5	15.06±2.4	-21.55±4.6
6	Ph	Ph	Ph	benzyl	181.77	11.22	10.18±0.36	9.43±0.33	-42.61±3.7
7	Ph	Me	Ph	benzyl	192.10	23.72	16.46±0.23	15.71±0.26	-24.28±1.6
8	Ph	Et	Ph	benzyl	8.11	25.04	17.88±0.33	17.14±0.32	-20.35±1.44
9	Ph	H	Ph	Me	45.70	2.82	18.33±0.25	17.59±0.24	-23.50±1.50
10	Ph	H	Ph	Et	8.40	0.52	21.07±1.7	20.33±1.6	-19.50±2.6
11	Ph	H	Ph	allyl	148.20	36.59	14.46±0.11	13.72±0.1	-28.80±1.7
12	Ph	H	Ph	2-pyridyl	0.80	0.049	2.17±0.09	1.43±0.06	-78.46±7.39
13	Ph	H	Ph	4-pyridyl	1.30	0.08	8.87±0.11	8.13±0.10	-59.54±3.85

As expected the k_2 values increase in the following sequence : 2-pyridyl$<$4-pyridyl

⟨ethyl⟨methyl⟨allyl⟨benzyl. These results show that the S_N2 reactions found for all substrates is accompanied by unimolecular ionisation for the 2- and 4-pyridyl derivatives. We interpret this as evidence for simultaneous S_N1 and S_N2 reactions between the corresponding substrates and the amines studied. The S_N1 to S_N2 mechanistic changeover has been the subject of considerable controversy;



5- R = H
6- R = Ph
7- R = Me
8- R = Et



9- R = Me
10- R = Et
11- R = Allyl
12- R = 2-Pyridyl
13- R = 4- Pyridyl

it has been proposed that substitutions, quite generally, proceed by initial ionisation[5] and alternatively that solvolysis generally proceeds with nucleophilic assistance of solvent[6]. Consideration of the compound set (5,9,10,11,12,13) shows that S_N2 rates for 11 and 12 decrease by factor of 6 and 4582 than that for 5, respectively, due to steric effect. The obtained results indicates that the transalkylation by 5,6-dihydro-2,4-diphenylnaphtho[1,2-b] pyridinium cations proceeds much faster than reactions utilising the 1-benzyl-2,4,6-triphenylpyridinium cations[3] as transalkylating agent. This may be attributed to the presence of the naphthyl maiety in the present compounds which assist release of the N-substituent by both steric and inductive effects.

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