SELECTIVE METHYLATION OF INTRAMOLECULAR N AND S GROUPS

— POSSIBLE FORMATION OF σ-AMMONIOSULFURANES —

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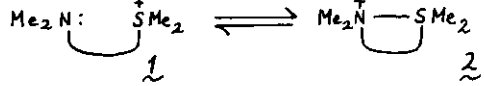
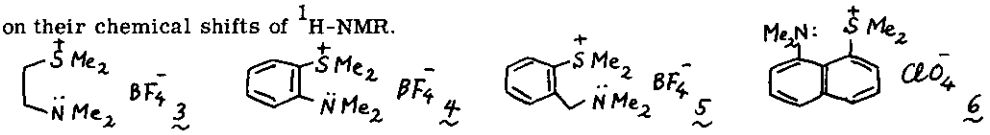
In the course of investigation on the selective methylation of intramolecular S and N groups, attention was focused on the interaction of the amino and the sulfonio groups which would yield σ-ammoniosulfuranes (2) in its ultimate (strong) stage as shown in eq. 1.



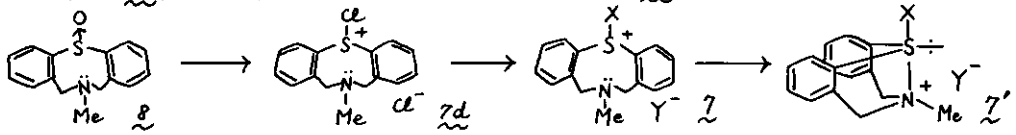
(1)

Several compounds were prepared as its model, but no meaningful interaction was observed based on their chemical shifts of ^{1}H-NMR.



These negative results were ascribed to frontal steric hindrance among four methyl groups of 3 - 6, therefore S-substituted N-methyl-6, 7-dihydro-5H-dibenzo[b, g][1, 5]thiazocinium salts (7) were prepared which would avoid such hindrance by taking trigonal bipyramidal structure (7').

The sulfoxide (8) was converted to 7d (X= Cl) with thionyl chloride and 7d was derived to 7c (X= OMe) and 7b (X= OEt) with sodium alkoxides and also to 7a (X= Me) with lithium dimethylcuprate.



The structure of 7d was concluded to be 7d' based on ^{1}H-NMR spectra. All 7 showed similar ^{1}H-NMR spectra assignable to TBP and plots of chemical shifts of the N-methyl group against Hammett substituent constants of X (σ_m and σ_I) gave very good straight lines, supporting dominance of TBP (7') for 7 :

$$\delta = 1.30\ \sigma_m + 2.68\ (r = 0.989,\ n = 5)\ ;\ \delta = 1.15\ \sigma_I + 2.60\ (r = 1.000,\ n = 4)$$

As far as we know, 7a is the first example of σ-sulfurane where the methyl group is attached at the apical position of TBP.