NEW ANALYSIS OF REACTIVITY AND REACTIONS OF NITROGEN-CONTAINING HETEROCYCLES

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I. New Analysis of Reactivity. In order to interpret ^{13}C-chemical shifts in both aliphatic and aromatic series, novel inductive and mesomeric substituent parameters, ι and μ, were proposed. Various spectral data and σ_J constants were correlated with $[a(\iota + b\mu) + c]$ $(b \geqq 0)$. Furthermore, novel effects such as 1,3-through space interaction, α- and β-lone pair effects and analogous behavior of C-H bond to C=C bond were proposed and various phenomena and reactivities were explained clearly.[1] The above equation and novel effects were shown to be useful as new method for analysis of reactivity in various kinds of amines.

II. N⋯S Interaction and Bond-Switch in 5-Amidino-1,2,4-thiadiazoles and Related Systems. Several examples of ring transformation have been reported, in which π-sulfurane intermediate seems to be invoked. It was found that formation of 1:1 adducts (1) from 5-imino-4,5-dihydro-1,2,4-thiadiazoles with nitriles or imidates accompany bond switch on the sulfur atom, and charge transfer interaction from the imino nitrogen atom to the sulfur atom was demonstrated by ^{13}C-NMR and X-ray crystallography.[2] Alkylation of 1 gave mono- and di-alkylated compounds successively and bond switch occurred in each step.[3] The 1:1 adducts (2) between 5-amino-3-methyl-1,2,4-thiadiazole and nitriles were shown to be equilibrated mixture of α- and β-isomers by NMR.[4] Even by protonation of 1, bond switch to protonated product (3) was observed and rapid equilibration between 1 and 3 was found by NMR.

Thus, it was demonstrated that bond switch occurs easily.

1) N. Inamoto, S. Masuda, Kagaku no Ryoiki, 33, 4, 105, 198 (1979); N. Inamoto, ibid., 303, 410, 495 (1979). 2) N. Inamoto, Kagaku (Kyoto), 33, 920 (1978); K. Akiba, S. Arai, T. Tsuchiya, Y. Yamamoto, F. Iwasaki, Angew. Chem. Int. Ed. Engl., 18, 166 (1979); K. Akiba, S. Arai, N. Inamoto, K. Yamada, H. Tanaka, H. Kawazura, Chem. Lett., 1978, 1415. 3) K. Akiba, S. Arai, F. Iwasaki, Tetrahedron Lett., 1978, 4117. 4) K. Akiba, T. Kobayashi, S. Arai, J. Am. Chem. Soc., in press.