〔Tetrahedron, **46**, 7393 (1990)〕

Hard Acid and Soft Nucleophile Systems. Part 12. Regioselective Functionalization of 1,3-Dienes through the Lewis Acid Mediated Thienium Cation Diels-Alder Reaction.

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In the Diels-Alder reaction, the electron-donating alkyl sulfenyl groups at the β-position of α-nitroalkenes may decrease the normal reactivity toward dienes. However, we found that the use of aluminium chloride in the attempted Diels-Alder reaction of β-ethylthio-α-nitroalkenes with 1,3-dienes dramatically changed the reaction course. The reaction led to the formation of *Z*-olefins by the regio- and stereoselective 1,4-funcfionalization of 1,3-dienes, which probably involve the Diels-Alder cycloaddition of a thienium cation intermediates, generated from the β-ethylthio-α-nitroalkenes, with the dienes.

〔J. Chem. Soc., Faraday Trans., **86**, 2971 (1990)〕

Physicochemical Properties of a Novel Nitrogen-containing Plasma-deposited Ultrathin Film.

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Amphiphilic nitrogen-containing ultrathin films have been formed by brief plasmolysis of various kinds of nitrogen-containing organic compounds such as amino-, amido-, nitrile- and nitro-derivatives. Ultrathin films prepared from nitrogen-rich organic compounds, however, have been found to induce neither effective polymerization of vinyl monomers nor spin adduct formation of PBN, unlike those from non-nitrogen-containing organic compounds. Most of these films were very unstable in solvents, and the nitrogen-containing moiety in the resulting films was readily leached out of the film into either polar or non-polar solvents.

〔J. Chem. Soc., Faraday Trans., **86**, 2975 (1990)〕

Effects and Role of Basic Nitrogen-derived Ultrathin Films on 'Plasma-Reduction'.

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Basic nitrogen-derived ultrathin films have been formed on brief plasmolysis (in a closed system) of even non-basic nitrogen-containing organic vapours such as dimethylformamide (DMF) and nitrile derivatives. The nitrogen-containing entity in these is readily leached into either polar or non-polar solvents. Based on these findings, the reported 'plasma reduction' of various electron-accepting compounds by energetic electrons could be rationalized in terms of nitrogen base-catalysed reactions, since various viologens, organic dye compounds, iodine and all other compounds reported for 'plasma reduction' also undergo electronic spectral changes in reactions with nitrogen bases.