

# Novel Asymmetrical Dianionic Polyimido-Sulfur(IV)-Ylides

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*Dedicated to Prof. Wolfgang Malisch on the occasion of his 60th birthday*

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Sulfurdiimides  $RN=S=NR$  react in donating solvents with two equivalents of lithiumalkyls to give the dimeric *C,N*-dilithium-methylenediimidosulfite solvent adducts  $[(Et_2O)Li_2\{H_2CS-(NSiMe_3)(N'Bu)\}]_2$  (**1**) and  $[(thf)Li_2\{H_8C_4S(N'Bu)_2\}]_2$  (**2**). Firstly, addition of a lithiumalkyl to sulfurdiimide gives the diimidosulfates  $[RS(NR')_2]^-$  (**1**:  $R = Me$ ,  $R' = 'Bu$ ,  $SiMe_3$ ; **2**:  $R = nBu$ ;  $R' = 'Bu$ ) while in a second step the  $\alpha$ -carbon atom in  $R$  is metalated with one equivalent of lithiumalkyl to give the asymmetric S-ylides. The reaction of 3-bromothiophene with one equivalent of  $nBuLi$  and one of sulfurdiimide  $'BuN=S=N'Bu$  resulted in the dilithium-3-thiophenylenediimidosulfite  $[(thf)Li_2\{(SC_4H_2)S(N'Bu)_2\}]_2$  (**3**). It can be regarded as the first example of a dianionic S(IV)- $\beta$ -ylide. This class of compounds can be rationalised as sulfite analogues, where two oxygen atoms are isoelectronically replaced by a  $NR$  group each and the remaining oxygen atom is replaced by a  $CR_2$  group. The rich coordination chemistry of the triimidosulfites is extended by the introduction of a hard carbanionic centre.

*Key words:* Chiral Auxiliaries, Sulfur Ylides, Wittig Reactions