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THE STEREOCHEMICAL OUTCOME OF DIENE ADDITIONS TO THIONITROSOARENES (ArN=S)

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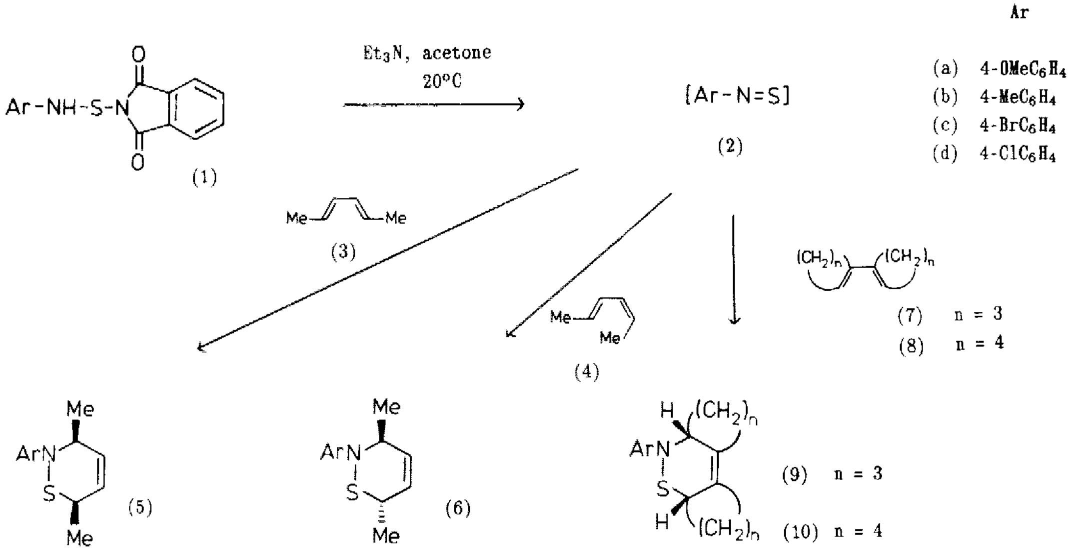
Abstract - Thionitrosoarenes (ArN=S) react efficiently with (E,E)- and (E,Z)-hexadienes to yield 1,2-thiazine adducts in which the stereochemistry of the diene is retained.

We have recently developed the first, straightforward method for the generation of thionitrosoarenes, ArN=S (2). These transient intermediates (2), generated from precursors (1), have been trapped as Diels Alder adducts with butadiene, isoprene and 2,3-dimethylbutadiene, and as ene adducts with alkenes.[1] Before the synthetic potential of RN=S species can be exploited, it is necessary to establish the stereochemical outcome of their addition reactions. The analogous chemistry of N-sulphinylamines (RN=S=O) and sulphodiimides (RN=S=NR) is developing rapidly.[2] For example, cycloadditions of (E,E)- and (E,Z)-hexadienes, (3) and (4), to these dienophiles show the usual Diels Alder syn stereoselectivity,[3] although the sterically overcrowded (Z,Z)-hexadiene reacts by a non-concerted mechanism with $PhSO_2N{=}S{=}O$.[3a,e] The structures of the cycloadducts (viz. dihydrothiazine-S-oxides and S-imines) from RN=S=O and RN=S=NR species are complicated by chirality at sulphur: a feature which is, of course, absent in RN=S adducts.

Thionitrosoarenes (2a) and (2c) reacted cleanly with (E,E)-hexadiene (3) (35 equivalents of diene) in acetone at 20°C to yield, in each case, a single, stereoisomeric product in >98% diastereomeric excess assigned the syn adduct structures (5a) and (5c), respectively (yields > 70%). These results establish the retention of sterochemistry in the addition reaction. Thionitrosoarenes (2a-d) reacted with the isomeric (E,Z)-diene (4) (35 equivalents) to yield the stereoisomeric products (6a-d), respectively. In all cases adducts (5a-d) were found alongside (6a-d) due to the presence of diene (3) as an impurity (<10% by g.c.) in samples of diene (4).[4] The more reactive thionitrosoarenes (2c) and (2d) yielded (6c) and (6d) in 90% d.e., whereas (2a) gave a 1:1 mixture of diastereoisomers (5a) and (6a).

Reaction of (2a) and (2c) with a 1:1 mixture of dienes (3) and (4) showed high selectivity in favour of the (E,E)-diene (3), giving (5a) in >96% d.e. and (5c) in 80% d.e. These results demonstrate the decreased reactivity (i.e. increased selectivity) associated with the electron donating substituent on the aryl group of ArN=S. The product mixtures from (2) and (4) were heated at reflux in chloroform for 16 h without changing the product distribution.

We have also reacted the tetrasubstituted dienes (7) and (8) with 1-methoxy-4-thionitrosobenzene (2a) and obtained adducts of single relative stereochemistry (>95% d.e.; ca. 70% isolated yields) for which all data are consistent with structures (9) and (10) respectively.[5]



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4. Percentage conversion for all reactions of (2) was >95% of which ca. 70% was isolated as cycloadducts (5) and (6): byproducts were tentatively identified as ArN=S=NAr and ArN=NAr derivatives. No ene adduct was detected by n.m.r. The integration of the methyl group doublets of adducts (5) and (6) was used to assign isomer ratios. Data for adducts (5a) and (6a) are representative: δ_H ($CDCl_3$) (5a) 1.44 (J = 6.64 Hz) and 1.08 (J = 7.18 Hz); (6a) 1.38 (J = 6.71 Hz) and 1.24 (J = 7.21 Hz) ppm.
5. The reaction of 1,1'-bicyclohexenyl (8) with $EtO_2CN=S=O$ yielded a single product (ref. 3e).

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