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A Novel Reaction of Aryl N-Sulphinylamines, Addition to 1,4-Naphthoquinone.

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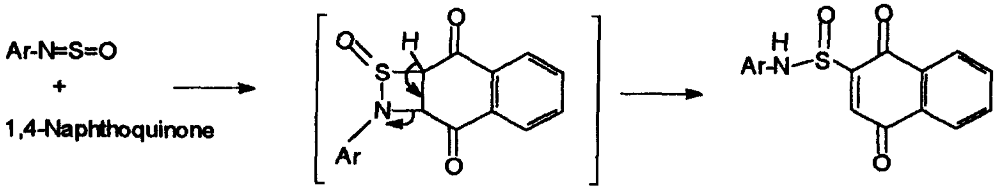
Abstract, Aryl N-sulphinylamines react with 1,4-naphthoquinone to give 2-arylsulphinoyl-1,4-naphthoquinones

Aryl N-sulphinylamines have attracted interest as important synthetic intermediates[1] This versatile heterocumulene undergoes a wide range of reactions These reactions include (4+2) cycloadditions with 1,3-dienes where the N=S bond acts as a dienophile[2-6], and reactions with strained alkenes where the N=S bond is a part of the diene. This second type of reaction is known only with a limited number of strained bicyclic alkenes[7-9] Attempts to extend this reaction as a general approach to 1,2-thiazine oxides, by using a wide range of alkenes of various electron densities and steric properties have failed so far[7,10,11] Other (4+2) cycloadditions of N-sulphinylamines are known with aromatic Schiff bases to give thiadiazine oxides[12]. Reactions with nitrones are believed to occur via a (3+2) cycloaddition[13], in which the primary adduct ring opened eliminating SO_2 Highly reactive sulphonyl sulphinylamines undergo (2+2) cycloaddition with enol ethers to yield 3-alkoxy-1,2-thiazetidine 1-oxide derivatives which are stable[14] The reaction N-alkyl Schiff bases with N-sulphinylamines takes a different route than the N-aryl compounds[12], this reaction is believed to occur via a (2+2) cycloaddition followed by the ring opening of the adduct

In our attempts to extend the scope of the N-sulphinylamine reactions, we have studied the reactions between 1,4-naphthoquinone and aryl N-sulphinylamines Reaction with 1,4-naphthoquinone is slower than the strained alkenes When an equimolar mixture of phenyl N-sulphinylamine and 1,4-naphthoquinone in beenzene is left at room temperature in the dark the solution turned into a deep red colour after 2-3 days The product was isolated after chromatography and further purified by recrystallization, yield 62%, as red crystals, m pt 186-9° Mass spectrum of this product showed a molecular ion at 297 corrosponds to an adduct The presence of N-H , C=O and S=O functions were evident from the IR spectrum The singlet peak at 6 43 in the ^{1}H NMR and ^{13}C peak at 103.35 corrosponds to one olefinic hydrogen and the attached carbon All the spectral data[15] are in full agreement with the proposed structure 2a. Formation of the 2-arylsulphinoyl-1,4-naphthoquinones can be explained by the mechanism shown, (2+2) cycloaddition of the N=S bond and the olefinic bond of the 1,4-naphthoquinone forms a 1,2-thiazetidine-1-oxide intermediate which readily frgments with a 1,3-H shift



1a,Ar = C_6H_5-   1b,Ar = o-CH_3-C_6H_4-   2a-d

1c,Ar = m-CH_3-C_6H_4-   1d,Ar = p-CH_3-C_6H_4-

This is a novel reaction of aryl N-sulphinylamines, and offers the first example of a reaction with an electron deficient, non strained alkene. Three other aryl N-sulphinylamines, also gave the similar adducts, 2b, yield 48%, m.pt 153-5°, 2c, yield 56%, m.pt 170-2°, and 2d, yield 68%, m.pt 190-1°

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15. 2a. Anal calcd for. $C_{16}H_{11}NSO_3$, C 64.63, H 3 73%.; found, C 64 52, H 3 78%.
   IR ($CHCl_3$) 3360 (NH), 1675 (C=O), 1614 (C=O), 1597, 1574, 1515, 1450, 1350, 1295, 1124 (S=O), 990 cm^{-1}.
   ^1H NMR ($CDCl_3$, 300MHz), 6.43 (1H s, C_3-H), 7 22 (1H, d,d, J=7.3, 8.0), 7 28 (2H, d, J=9 0),
   7.42 (2H, d,d, J=7 5, 8 3) 7.58 (1H, bs, NH), 7.67 (1H, d,t, J=1.3 7 7), 7 76 (1H, d,t, J=1.3, 7 7),
   8 11 (1H, d,d, J=1.3, 7 5), 8.13 (1H, d,d, J=1 3, 7 5)., ^{13}C ($CDCl_3$, 75MHz), 103 35 (C_3), 122 59 (2xC), 125.61, 126 15, 126 52, 129 68 (2xC), 130 33, 132 35, 133.19, 134.92, 137.41, 144 69, 182.06 (C=O), 183.95 (C=O).
   MS, m/e, M^+ 297 (4), 249 (57, M^+-SO), 220 (32, M^+-Ph), 204 (18, M^+-$PhNH_2$), 193 (11), 165 (14), 144 (26), 104 (61), 77(100)

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