# Ring Opening of the Benzothiazole System

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*Summary* 6-Nitrobenzothiazole reacts reversibly with methoxide ion at room temperature in $Me_2SO$ giving an anionic adduct which with MeI or $Br_2$ and pyridine in $CCl_4$ yields 2-methoxymethyleneamino-5-nitrophenyl methyl sulphide and bis-(2-methoxymethyleneamino-5-nitrophenyl) disulphide, respectively.

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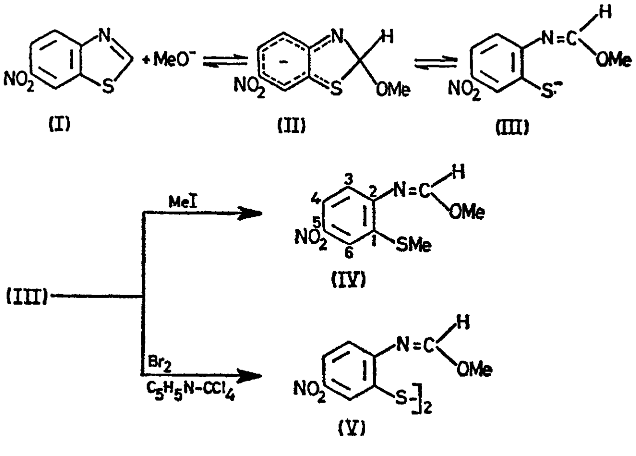
IN reported examples of ring opening of neutral heteroaromatic compounds by the action of bases under mild conditions irreversible cleavage occurs.[1] We report here that the reaction of 6-nitrobenzothiazole (I) with methoxide ion at room temperature in $Me_2SO$ reversibly leads to an anionic adduct which with electrophilic reagents yields the ring-opened derivatives originating from S–C(2) bond cleavage.

Thus, when a 0·1M solution in $Me_2SO$ of (I) was mixed with an equimolecular solution of $MeO^-$ a dark red colour developed immediately ($\lambda_{max}$ 510 nm). Subsequent addition of a stoicheiometric amount of MeI or $Br_2$ and pyridine in $CCl_4$ solution quantitatively yields compounds (IV) and (V) respectively. These structures were assigned on the basis of C,H,N analysis and $^1H$ n.m.r. spectra [*e.g.* for (IV) $\tau$ (60MHz, $CDCl_3$) 2·13—2·33 (2H, m, 4- and 6-H), 2·45 (1H, s, N=CH), 3·32 (1H, d, 3-H), 6·10 (3H. s, –OMe), and 7·55 (3H, s, –SMe)].

Moreover, if aqueous acetic acid is added to the red mixture, (I) is quantitatively regenerated. As expected, the equilibrium was influenced by the initial concentration of reagents.

These results suggest that reversible nucleophilic attack of the base on C-2 occurs probably leading to (II) and/or (III) (Scheme). The $^1H$ n.m.r. spectra of the red mixture showed all resonances shifted to higher field with respect to (I). From coupling-constant data and the spectra of the 2-deuterio-compound the following assignments could be made: for (I), $\tau$ [60 MHz, $(CD_3)_2SO$] 0·42 (1H, s, 2-H), 0·93 (1H, m, 7-H), and 1·80 (2H, m, 4- and 5-H); for the adduct, 2·15 (1H, d, 7-H), 2·66 (1H, dd, 5-H), 3·62 (1H, d, 4-H), and 4·56 (1H, s, 2-H). The 2-H resonance in the adduct is more consistent with a Meisenheimer-like complex (II) in agreement with the $sp^3$ hybridization of C-2. N=C–*H* in (III) should probably resonate at lower field as is also suggested by comparison with the n.m.r. spectra of (IV) and (V).



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However, the rapid formation of ring-opened compounds does not rule out the presence of a small amount of (III) in equilibrium with (II), since detection of the ring-opened anionic adduct is difficult owing to the low solubility of (I) and also signals from (III) could be hidden by those from (II).

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