Homolytic Aromatic *Ipso* Substitutions in Benzothiazoles by the Nucleophilic 1-Adamantyl Radical[1]

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Summary 1-Adamantyl radicals react with several 2-substituted benzothiazoles to afford 2-(1-adamantyl)-benzothiazole as a result of a homolytic substitution occurring at the *ipso* position; the yields are greater when the groups to be displaced are electron-withdrawing.

THE recently reported displacement reactions of the cyano-[2] and acyl-groups[3,4] by nucleophilic carbon radicals in hetero-aromatic compounds prompted us to report our results on the reactions of several 2-substituted benzothiazoles resulting in the replacement of the substituents by the 1-adamantyl (Ad•) radical.

Ad• and other nucleophilic alkyl radicals react with acylpyridines,[3] acylquinolines,[3,4] and 2-acylbenzothiazoles[3,4] effecting the displacement of the acyl group in good yields. Electron-withdrawing substituents in the 5- and 6-positions of 2-acetylbenzothiazole facilitate the substitution process.[5] In this case, relative reactivity data suggested that this displacement can be regarded as an aromatic S_R reaction occurring at the *ipso* position with a significant contribution of the polar forms (II) in the transition state of the addition step, owing to the electron affinity of the substrate and the nucleophilic character of the attacking radical. A closely related mechanism has been proposed for the displacement occurring in protonated quinolines.[4]

The synthetic as well as the theoretical interest of these reactions induced us to extend our investigation and we now report that the displacement reaction is not limited to the acyl group. In a typical example, an aqueous solution (15 ml) of $(NH_4)_2S_2O_8$ (30 mmol) was added dropwise to a stirred mixture, at 80 °C, of 2-phenylsulphonylbenzothiazole (I, X = $PhSO_2$) (10 mmol), adamantane-1-carboxylic acid (25 mmol), and $AgNO_3$ (1 mmol) in 5% aq. NH_3 (35 ml) and MeCN (35 ml). At the end of the addition the starting sulphone was completely converted and 2-(1-adamantyl)benzothiazole (IV) was isolated in 80% yield.

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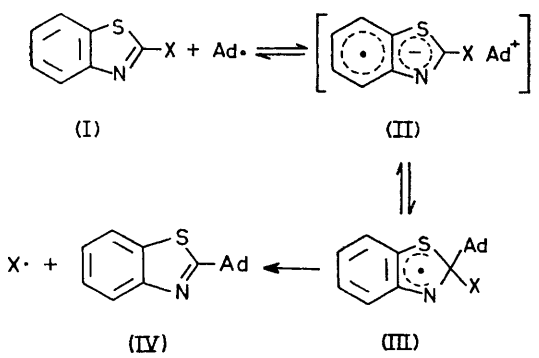
Similar results were obtained with the 2-sulphinyl- and 2-acylbenzothiazoles; under the same conditions the 2-methylthio-, 2-methoxy-, and 2-halogeno-benzothiazoles were only partially converted and lower yields of (IV) were obtained.



SCHEME. X = $PhSO_2$ (100%, 80%); PhSO (100, 80); PhCO (100, 55) (ref. 5); MeCO (100, 60) (ref. 5); HCO (100, 40) (ref. 5); MeS (50, 60); MeO (10, 40); Br (50, 70); Cl (40, 50); F (40, 50). Figures in parentheses refer to the amount of (I) which had reacted and yields of (IV) based on converted (I) respectively. Reaction mixtures were analysed by g.l.c. and products separated by column chromatography. All compounds are described in the literature.

The results in the Scheme indicate that the reaction occurs more easily when the group X is electron-withdrawing. On the basis of these purely qualitative results it is suggested that these *ipso* substitution reactions occur by the addition–elimination sequence indicated in the Scheme; the polar forms (II) play an important role in determining the ease of formation of the σ-complex intermediate (III).[4,5] The fate of (III) is then influenced by the nature of X. In principle several paths are available to this radical: (i) loss of X resulting in the substitution of a radical for another, *i.e. ipso* substitution; (ii) loss of Ad• and return to starting materials; (iii) fragmentation, by homolytic fission of the C(2)–S bond, hydrogen abstraction, (v) loss of a group from a substituent remote from the *ipso* position and (vi) coupling with other radicals or dimerization, to afford products of different nature. The only process identified so far is *ipso* substitution, but the different fates of (III) might be responsible for the low yields of conversion encountered in some cases.

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[1] The prefix *ipso* is employed here to denote the position bearing the substituent, as suggested by C. L. Perrin and G. A. Skinner, *J. Amer. Chem. Soc.*, 1971, **93**, 3389.

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