Ipso Substitution in the Reaction of Acyl Radicals with 2-Substituted Benzothiazoles[1]

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Summary Nucleophilic acetyl radicals react with 2-substituted benzothiazoles effecting the displacement of several groups to afford 2-acetylbenzothiazole; the reactions are proposed to occur through a homolytic aromatic substitution at the *ipso* position.

THE homolytic alkyl-deacylation reaction occurring in the pyridine,[2] quinoline,[2,3] and benzothiazole[2,4] systems has received considerable attention recently. Several other groups have also been found to be easily substituted by the nucleophilic 1-adamantyl radical.[4] Moreover, an interesting example of another displacement reaction, acyl-deacylation, has also been observed.[3] Our present results demonstrate that displacement by acyl radicals is quite a general process, many other substituents being replaced by these nucleophilic radicals.

Acetyl radicals, produced from Bu^tOOH (40 mmol), $FeSO_4$ (40 mmol, in 35 ml H_2O) and MeCHO[5] (0·1 mol) react with 2-substituted benzothiazoles (2-BTR) (I) (10 mmol), in acetic acid (50 ml), to give 2-acetylbenzothiazole (2-BTAc) (III); the product was separated by column chromatography and the yields, based on converted (I), are reported in the Table.

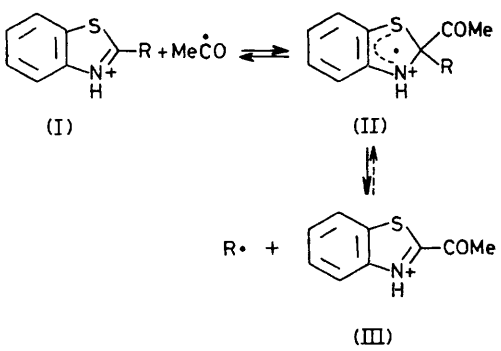

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TABLE

2-BTR + MeĊO ⟶ 2-BTAc + R·
(I) (III)

R	% Conversion of (I)	% Yields of (III)
$PhSO_2$	90	75
PhSO	90	75
EtCO	90	73
PhS	76	36
F	70	26
Cl	60	5

The results reported here represent further examples of the ease with which homolytic aromatic *ipso* substitutions can occur in the benzothiazole system.[4] The addition–elimination mechanism in the Scheme, proposed for the displacement of the acyl group,[3] most probably operates in the present case also.

Both steps have been formulated as reversible; this however may not hold for all the reactions examined, but is presumably limited to the case of R = COX groups. The other displaced radicals R, in fact, do not exhibit nucleophilic properties and their reactions with (III) therefore should not be favoured.

Protonation of the substrates (I) facilitates the *ipso* attack of the acetyl radical to give the σ-complex intermediate (II) and the conversion yields are consequently very high in every case. The yields of the *ipso* substitution product (III), however, are rather low when R = PhS, F, or Cl, indicating that, in these cases, the intermediate (II) [or perhaps (I)] is concurrently involved in other processes.[4]

We thank the C.N.R. Rome for financial support.

(*Received*, 31*st January* 1977; *Com.* 077.)

[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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[3] T. Caronna, A. Citterio, and M. Bellatti, *J.C.S. Chem. Comm.*, 1976, 987. (We thank Dr. A. Citterio for having provided us with a copy of the manuscript prior to publication).
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