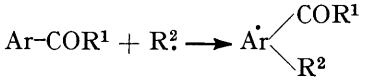
# Displacement of the Acyl Group in Benzothiazoles by Nucleophilic Alkyl Radicals. Homolytic Aromatic *ipso*-Substitution [1]

By **Michele Fiorentino, Lorenzo Testaferri,† Marcello Tiecco,*†** and **Luigino Troisi,** Istituto di Chimica Organica, Via Amendola 173, Bari, Italy

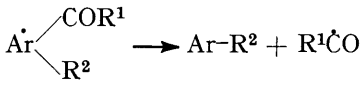
1-Adamantyl and other alkyl radicals, produced by the $Ag^{I}$ catalysed decarboxylation of carboxylic acids by ammonium peroxydisulphate, react with 2-acylbenzothiazoles effecting the displacement of the acyl group to afford 2-alkylbenzothiazoles in good yield. The reaction with 1-adamantyl radicals is facilitated by the presence of electron-withdrawing substituents in the 5- and 6-positions of the benzothiazole nucleus. The displacement process is regarded as an aromatic $S_R$ reaction occurring at the *ipso*-position.

It has recently been observed that 1-adamantyl (Ad·) and other nucleophilic alkyl radicals, besides giving the usual homolytic aromatic substitution reactions,[2] are also capable of effecting the displacement of acyl groups in the pyridine, quinoline, and benzothiazole systems.[3,4] On the basis of spectroscopic evidence a mechanism was proposed by us, in the case of acetylpyridines, which implied the initial formation of the 4-acetylpyridine radical cation;[4] support for this hypothesis came from the fact that the reaction occurred more easily with the free bases than with their protonated forms. The effect of substituents however could not be fully investigated. In a more recent investigation of the same system, in acidic media,[5] it was suggested that the mechanism proposed for the homolytic substitution of protonated heteroaromatic bases [6] also operates in the displacement of the acyl group by alkyl radicals.[4]

We report here results on the reactivity of substituted 2-acetylbenzothiazoles with alkyl radicals. Relative reactivity data showed that, in this system, the displacement of the acetyl group by Ad· is effected by substituents in the same way as the displacement of hydrogen in the corresponding benzothiazoles. In the light of these results we suggest that the process can be regarded as a homolytic aromatic substitution occurring at the *ipso*-position,[7] *i.e.* a two-step process involving an addition–elimination sequence similar to that generally accepted for the substitution of hydrogen [reactions (1) and (2)].



(1)



(2)

## RESULTS AND DISCUSSION

1-Adamantyl and other alkyl radicals were produced by the $Ag^{I}$ catalysed decarboxylation of the corresponding carboxylic acids by ammonium peroxydisulphate [reactions (3)—(6)].[8] The reactions were carried out in aqueous basic solution in the presence of acetonitrile to

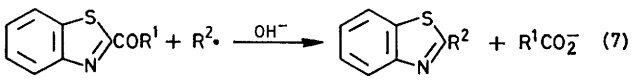
$$S_2O_8^{2-} + Ag^+ \longrightarrow SO_4^{-\cdot} + SO_4^{2-} + Ag^{2+} \quad (3)$$

$$SO_4^{-\cdot} + Ag^+ \longrightarrow SO_4^{2-} + Ag^{2+} \quad (4)$$

$$Ag^{2+} + RCO_2^- \longrightarrow Ag^+ + RCO_2\cdot \quad (5)$$

$$RCO_2\cdot \longrightarrow R\cdot + CO_2 \quad (6)$$

ensure complete solubility of the 2-acylbenzothiazoles (I). In order to obtain the maximum conversion of (I) into the 2-alkylbenzothiazoles (II), an excess of the carboxylic acids and of the oxidizing agent was generally employed; nevertheless some unchanged (I) were recovered in many cases. In no case were other products derived from the benzothiazole nucleus identified. From the reactions of 2-benzoylbenzothiazoles with Ad·, besides the substitution products (II), benzoic acids were also isolated indicating that the leaving acyl group is converted, at least in part, into the corresponding carboxylic acid [reaction (7)].



(I) (II) (7)

Other reactions of the alkyl radicals were observed to occur concurrently with the displacement process. From the experiments carried out with Ad·, adamantane and adamantan-1-ol were isolated; their formation can confidently be attributed to hydrogen abstraction and to oxidation [2] followed by nucleophilic capture of the 1-adamantyl cation by water, respectively. A more interesting by-product, which was isolated in considerable yield, was identified as 1-acetyladamantane (III). As it has been shown from independent experiments, this ketone forms by addition of Ad· to acetonitrile as suggested in Scheme 1. This reaction can have some synthetic importance. From the reaction carried out in the absence of the acylbenzothiazoles (I), the ketone

† *Present address:* Istituto di Chimica Organica, Facoltà di Farmacia, Perugia, Italy.

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[2] L. Testaferri, M. Tiecco, P. Spagnolo, P. Zanirato, and G. Martelli, *J.C.S. Perkin II*, 1976, 662.

[3] M. Fiorentino, L. Testaferri, M. Tiecco, and L. Troisi, *J.C.S. Perkin II*, 1977, 87.

[4] M. Fiorentino, L. Testaferri, M. Tiecco, and L. Troisi, *J.C.S. Chem. Comm.*, 1976, 329.

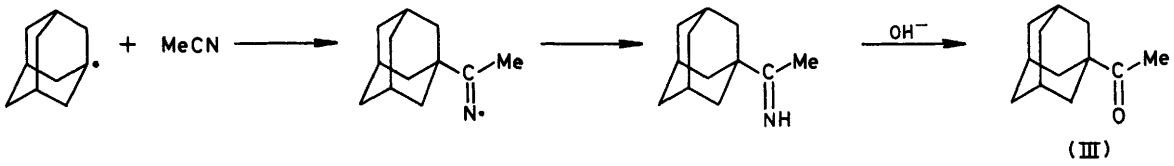
[5] T. Caronna, A. Citterio, and M. Bellatti, *J.C.S. Chem. Comm.*, 1976, 987 (we thank Dr. A. Citterio for having provided us with a copy of the manuscript prior to publication).

[6] F. Minisci, *Topics Current Chem.*, 1976, **62**, 1.

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

[8] J. M. Anderson and J. K. Kochi, *J. Amer. Chem. Soc.*, 1970, **92**, 1651; F. Bertini, T. Caronna, R. Galli, F. Minisci, and O. Porta, *Chimica e Industria*, 1972, **54**, 425.

(III) was in fact isolated in *ca.* 50% yield based on the adamantane-1-carboxylic acid employed. Addition of nucleophilic carbon radicals to the cyano-group represents an interesting process which has been observed previously to occur between cyclohexyl radicals and benzonitrile.[9]



SCHEME 1

TABLE 1

Yields of 2-alkylbenzothiazoles (II) obtained from the reaction of 2-acylbenzothiazoles (I) with alkyl radicals

| Acyl group in (I) | Alkyl radical | Yield (%) of (II) * |
|---|---|---|
| CHO | Ad· | 40 |
| Ac | Ad· | 60 |
| COEt | Ad· | 60 |
| Bz | Ad· | 55 |
| $COC_6H_4Cl$-*p* | Ad· | 56 |
| $COC_6H_4Me$-*p* | Ad· | 52 |
| $COC_6H_4OMe$-*p* | Ad· | 50 |
| Ac | Et(Me)CH· | 30 |
| Ac | $Me_2CH$· | 32 |
| Ac | $Me_3C$· | 25 |
| Ac | Me· | 9 |
| Ac | 1,4-Dioxan-2-yl | 30 † |

* Yields based on the acetylbenzothiazoles employed. † The dioxanyl radical was produced from dioxan.

In order to obtain information on the field of application of this alkyldeacylation reaction, several experiments were carried out. The results obtained are collected in Table 1. It can be observed that formyl-, acetyl-, propionyl-, and substituted benzoyl-benzothiazoles all react with Ad· to give satisfactory yields of the displacement product (II); under the same experimental conditions, other alkyl radicals also give rise to the displacement of the acetyl group, although in considerably lower yield.

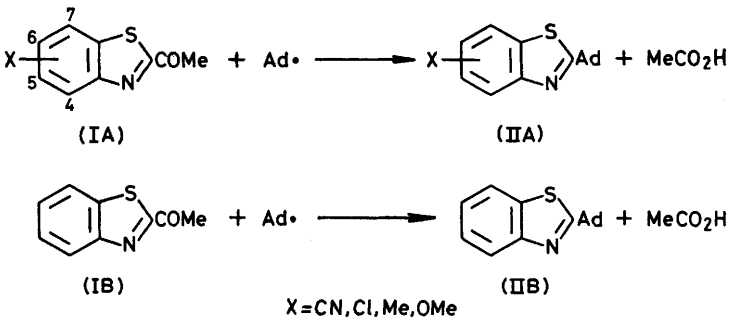
Displacement of the acyl group in 2-acetyl- and 2-benzoyl-benzothiazoles occurred equally well when Ad· were produced by the thermal decomposition of the t-butyl adamantane-1-percarboxylate in acetonitrile, indicating that the reaction is not influenced by the radical source employed.

The reaction of the 2-acetylbenzothiazole with Ad· was selected for deeper scrutiny of this displacement process. For this purpose the effect of substituents, with different electronic properties, on the rate of substitution was investigated. The reactivity of 5- and 6-substituted 2-acetylbenzothiazoles (IA) relative to the unsubstituted compound (IB) were determined using the competitive method. Working with an excess of an equimolecular mixture of the two substrates (IA and B), the ratio of the formed 5- or 6-X-2-(1-adamantyl)benzothiazole and 2-(1-adamantyl)benzothiazole, (IIA) : (IIB), is assumed to give directly the value of the relative reaction rate $K_{Ac}$. The results of these experiments are collected in Table 2.

TABLE 2

Relative rates of displacement of the acetyl group in 5- and 6-X-2-acetylbenzothiazoles ($K_{Ac}$), and of substitution in 5- and 6-X-benzothiazoles ($K_H$) by 1-adamantyl radicals

| | Relative rates | |
|---|---|---|
| Substituent X | $K_{Ac}$ | $K_H$ |
| 6-CN | 10.92 | 5.52 |
| 5-CN | | 3.20 |
| 6-Cl | 2.30 | 1.76 |
| 5-Cl | 2.18 | 2.00 |
| 5-OMe | 1.26 | 1.15 |
| 5,6-H | 1.00 | 1.00 |
| 5-Me | 0.86 | 0.88 |
| 6-Me | 0.60 | 0.72 |
| 6-OMe | 0.46 | 0.66 |



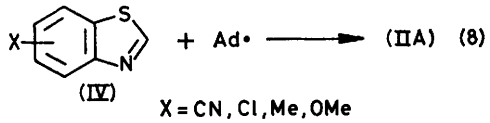
SCHEME 2

A satisfying Hammett correlation was observed using $\sigma_p$ values for the substituents in the 6-position and $\sigma_m$ values for those in the 5-position ($\rho$ 1.4; $r$ 0.98).

[9] J. R. Shelton and C. W. Uzelmeier, *J. Amer. Chem. Soc.*, 1966, **88**, 5222; J. R. Shelton and C. W. Uzelmeier, *Rec. Trav. chim.*, 1968, **87**, 1211.

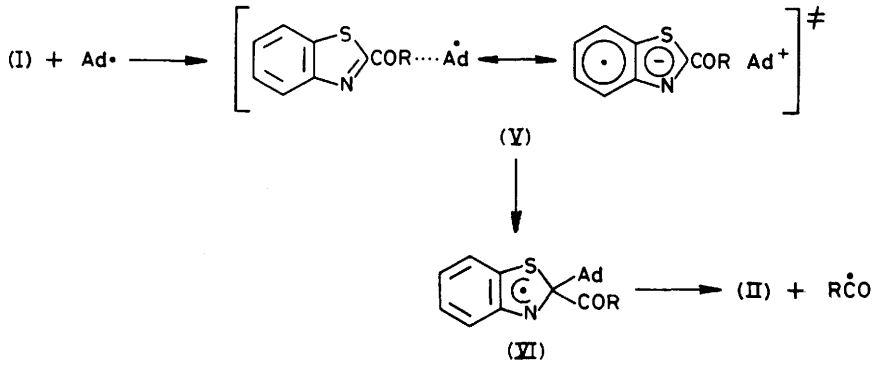
This implies that the effect of substituents is mainly transmitted through the nitrogen atom with little intervention by the sulphur atom; such behaviour seems to be a peculiarity of the benzothiazole nucleus and has already been demonstrated in the nucleophilic substitution reactions of the 2-halogenobenzothiazoles.[10]

The relative reactivity data indicate that electron-withdrawing substituents increase and electron-releasing substituents decrease the reactivity of 2-acetylbenzothiazole towards the 1-adamantyl radical. This trend is similar to that observed for substitution by the same radical in benzene derivatives,[2] and in 4-substituted protonated pyridines,[3] as well as to that presented by other nucleophilic alkyl radicals.[6,11] As a matter of fact, substituents in the 5- and 6-positions of benzothiazole (IV) act in the same direction in 1-adamantylation of benzothiazole, which also takes place selectively at the 2-position [reaction (8)].




The values of the relative rates ($K_H$) for these reactions were determined by competitive experiments, as described above for the 2-acetyl derivatives, and are collected in Table 2. A Hammett correlation (ρ 0.9; $r$ 0.98) was also observed in this case; the lower ρ value indicates less pronounced sensitivity to substituents effects than in the case of the 2-acetylbenzothiazoles. The values of the relative reactivities $K_H$ correlate linearly with the chemical shifts of protons in the 2-position of benzothiazoles (slope 2.29; $r$ 0.97). Similar correlations were already observed for the reactions of Ad·[3] and other alkyl radicals[11] with 4-substituted protonated pyridines and suggest that an important factor controlling the chemical reactivity is the electron density at the nuclear position suffering attack by the nucleophilic radical.[6,11] Interestingly a similar correlation also holds for the values of $K_{Ac}$ (slope 3.36; $r$ 0.98).

The close similarity of the two reactions of Ad· radicals with benzothiazoles and with 2-acetylbenzothiazoles suggests that a similar mechanism is operating (it is relevant in this respect that a plot of log $K_{Ac}$ against log $K_H$ gives a straight line with $r$ 0.99). The effect of substituents discussed above justifies the suggestion that the adamantyldeacetylation of benzothiazoles occurs through a mechanism similar to that proposed for the reaction of nucleophilic carbon radicals with protonated pyridines[3,11] and with electron-deficient benzene derivatives,[2] as also suggested by Gittezio *et al.*[5] for the alkyldeacylation of protonated quinolines. Thus, in the rate-determining step, the Ad· radical adds to the substrates to afford a σ-complex intermediate (VI) as a result of the attack at the *ipso*-position (Scheme 3); owing to the donor character of the radical and the acceptor capability of the substrate considerable charge separation should develop in the transition state (V) of this addition, thus explaining the observed effect of substituents. The substitution product (II) can then be formed, in the elimination step, by homolytic fission of the C–COR bond, although a preliminary oxidation to the corresponding cation cannot in principle be ruled out. This mechanism suggests that other nucleophilic radicals might be capable of effecting the same displacement and also that other substituents can facilitate the addition step and act as good leaving groups;[12] other electron-deficient aromatic substrates should present similar behaviour.




SCHEME 3

Attack at the *ipso*-position, resulting in *ipso*-substitution, is a well known process in electrophilic[7] and nucleophilic aromatic substitution and from the foregoing discussion it can be expected that it can commonly be observed in homolytic substitution also. Owing to the considerably greater reactivity of the 2-position with respect to the other nuclear positions, benzothiazole is a particularly suitable substrate to investigate the factors governing these $S_R$ reactions and work is presently in

[10] P. E. Todesco and P. Vivarelli, *Gazzetta*, 1962, **92**, 1221.
[11] F. Minisci, R. Mondelli, G. P. Gardini, and O. Porta, *Tetrahedron*, 1972, **28**, 2403.
[12] M. Fiorentino, L. Testaferri, M. Tiecco, and L. Troisi, *J.C.S. Chem. Comm.*, 1977, 316.

progress in this direction. Some examples are already available in the literature,[13] but they are mainly concerned with the displacement of halogen atoms by halogen,[14] aryl,[15] and cyclohexyl [9] and benzenesulphonyl radicals.[16] Some radical rearrangements also involve σ-complex intermediate of the same type as (VI) and can be seen as examples of intramolecular attack at the *ipso*-position; the attacking species can be a carbon [17] ($ArCR_2[CH_2]_2CH_2^{\bullet} \longrightarrow Ar[CH_2]_3CR_2^{\bullet}$; $^{\bullet}C_6H_4CONAr_2 \longrightarrow ArC_6H_4CONAr$), silicon [18] ($Ar[CH_2]_4SiMe_2^{\bullet} \longrightarrow ArSiMe_2[CH_2]_3CH_2^{\bullet}$), or an oxygen [19] centred radical ($o$-$C_6H_5OC_6H_4CO_2^{\bullet} \longrightarrow {}^{\bullet}OC_6H_4CO_2C_6H_5$) and the displacement occurs by carbon–carbon, carbon–nitrogen, and carbon–oxygen bond fission.

## EXPERIMENTAL

G.l.c. analyses were performed on a Hewlett–Packard 5700 instrument equipped with a flame ionization detector, using a 10% silicone GE XE 60 on Aeropak 30 (100—120 mesh) column. Quantitative analyses were effected with internal standards and calibration for area response differences was carried out for each reaction using pure samples of the various substituted 2-(1-adamantyl)benzothiazoles. Products characterization was accomplished by elemental analyses, 100 MHz n.m.r. spectroscopy (Varian HA 100), and i.r. spectroscopy (Perkin-Elmer 257).

*Materials.*—6-Cyano-,[20] 6-chloro-,[21] 6-methyl-,[21] 6-methoxy-,[21] 5-cyano-,[22] 5-chloro-,[21] 5-methyl-,[21] and 5-methoxy-benzothiazoles [21] were prepared as described in the literature. In many cases however we found it more convenient to effect deamination of 2-aminobenzothiazoles by aprotic diazotization in tetrahydrofuran.[23]

2-Formylbenzothiazole was prepared by metallation of benzothiazole with n-butyl-lithium at −60°, and subsequent treatment with *NN*-dimethylformamide at −40°; the mixture was worked-up in the usual way and the pure product was obtained by column chromatography on silica gel, m.p. 73—74° (lit.,[24] 75—76°). The other 2-acylbenzothiazoles (Table 1) were prepared by acylation of benzothiazole.[25] 5- and 6-substituted 2-acetylbenzothiazoles were similarly obtained from the benzothiazoles and acetaldehyde; their physical, spectral, and analytical data are collected in Table 3.

TABLE 3

Physical, spectral,[a] and analytical data of 5- and 6-X-2-Y-benzothiazole

| Compound | | | Chemical shift (δ) | | | | | Coupling constant (Hz) | | | | | Analysis (%) Found | | | Calc. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| X | Y | M.p. (°C) | 2 | 4 | 5 | 6 | 7 | $J_{4,5}$ | $J_{4,6}$ | $J_{4,7}$ | $J_{5,7}$ | $J_{6,7}$ | C | H | N | C | H | N |
| 5-CN | COMe [b] | 196—198 [c] | 2.80 | 8.5 | | 7.75 | 8.1 | | 1.3 | 0.5 | | 8.5 | 59.5 | 3.1 | 13.85 | 59.4 | 3.0 | 13.85 |
| 5-Cl | COMe [b] | 152—153 [c] | 2.70 | 8.05 | | 7.4 | 7.85 | | 2.5 | 0.75 | | 8.5 | 50.8 | 2.95 | 6.9 | 51.05 | 2.85 | 6.6 |
| 5-Me | COMe [b] | 101—103 [d] | 2.68 | 7.85 | 2.52 [j] | 7.25 | 7.75 | *l* | 2.65 | 0.85 | | 8.5 | 62.1 | 4.8 | 7.25 | 62.8 | 4.75 | 7.3 |
| 5-OMe | COMe [b] | 115—117 [e] | 2.65 | 7.45 | 3.83 [k] | 7.05 | 7.7 | | 2.2 | 0.5 | | 8.7 | 57.8 | 4.4 | 6.8 | 57.9 | 4.4 | 6.75 |
| 6-CN | COMe [b,h] | 200—201 | 2.83 | 8.25 | 7.8 | | 8.35 | 8.7 | | 0.8 | 1.5 | | 60.0 | 2.9 | 13.75 | | | |
| 6-Cl | COMe [b] | 159—160 [d] | 2.68 | 8.0 | 7.45 | | 7.85 | 8.8 | | 0.8 | 2.15 | | 51.1 | 2.75 | 6.5 | | | |
| 6-Me | COMe [b] | 102—103 | 2.65 | 7.9 | 7.25 | 2.50 [j] | 7.6 | 8.6 | | 0.85 | 2.25 | *n* | 63.1 | 4.8 | 7.3 | | | |
| 6-OMe | COMe [b] | 145—146 [d] | 2.64 | 7.9 | 7.05 | 3.84 [k] | 7.25 | 8.4 | | 0.5 | 2.5 | | 57.4 | 4.4 | 6.9 | | | |
| H | Ad | 82—84 [d] | *i* | 7.7 | 7.25 | 7.25 | 7.7 | *m* | | | | | 75.4 | 7.2 | 5.1 | 75.8 | 7.1 | 5.2 |
| 5-CN | Ad | 147—149 [c] | *i* | 8.05 | | 7.45 | 7.85 | | 1.6 | 0.7 | | 8.3 | 72.9 | 6.4 | 9.2 | 73.45 | 6.15 | 9.5 |
| 5-Cl | Ad | 95—97 [e] | *i* | 7.75 | | 7.2 | 7.65 | | 2.0 | 0.7 | | 8.4 | 67.6 | 6.2 | 4.7 | 67.2 | 6.0 | 4.6 |
| 5-Me | Ad | 65—66 [d] | *i* | 7.55 | 2.43 [j] | 7.0 | 7.55 | *l* | 2.0 | 0.6 | | 8.1 | 76.2 | 7.6 | 5.0 | 76.25 | 7.5 | 4.95 |
| 5-OMe | Ad | 70—71 [e] | *i* | 7.25 | 3.76 [k] | 6.8 | 7.5 | | 2.5 | 0.5 | | 8.6 | 72.3 | 7.0 | 4.7 | 72.2 | 7.1 | 4.7 |
| 6-CN | Ad | 184—186 [f] | *i* | 7.9 | 7.55 | | 8.0 | 8.1 | | 0.6 | 1.6 | | 72.9 | 6.15 | 9.8 | | | |
| 6-Cl | Ad | 158—159 [d,g] | *i* | 8.0 | 7.45 | | 7.85 | 8.7 | | 0.9 | 2.1 | | 67.6 | 6.0 | 4.7 | | | |
| 6-Me | Ad | 130—131 [d] | *i* | 7.65 | 7.1 | 2.42 [j] | 7.45 | 8.2 | | 0.7 | 2.2 | *n* | 76.4 | 7.3 | 4.9 | | | |
| 6-OMe | Ad | 119—120 [d] | *i* | 7.6 | 6.85 | 3.77 [k] | 7.1 | 8.8 | | 0.6 | 2.5 | | 73.0 | 7.05 | 4.5 | | | |

[a] 100 MHz n.m.r. spectra in $CS_2$. [b] $\nu_{max.}$ 1 695 $cm^{-1}$ ($CS_2$). [c] From hexane. [d] From light petroleum (b.p. 40—60°). [e] From light petroleum (b.p. 100—120°). [f] From ethanol. [g] Lit.,[21] 160°. [h] N.m.r. spectrum in $CDCl_3$. [i] 1-Adamantyl group, δ 1.82br (6 H, s, δ-H) and 2.1br (9 H, s, β- and γ-H). [j] Methyl group. [k] Methoxy group. [l] $J_{4,Me} = J_{6,Me} = 0.5$ Hz. [m] Not analysed. [n] $J_{5,Me} = J_{7,Me} = 0.75$ Hz.

A final comment concerns the mechanism of displacement in the acetylpyridines.[4,5] In our opinion, a decision on whether the reaction proceeds through a radical cation or through a mechanism similar to that discussed for benzothiazole must await the results of a more careful investigation; knowledge of the effect of substituents on the relative reaction rates should provide decisive information in this respect.


[13] M. J. Perkins, ' Free Radicals,' ed. J. K. Kochi, Wiley, New York, 1973, vol. II, p. 231.

[14] B. Miller, and C. Walling, *J. Amer. Chem. Soc.*, 1957, **79**, 4187; B. Milligan, R. L. Bradow, J. L. Rose, H. E. Hubbert, and A. Roe, *ibid.*, 1962, **84**, 158; J. T. Echols, V. T. Chuang, C. S. Parrish, and B. Milligan, *ibid.*, 1967, **89**, 4081; M. Nakashima, Chup Yew Mok, and R. M. Noyes, *ibid.*, 1969, **91**, 7635.

[15] P. A. Claret, G. H. Williams, and J. Coulson, *J. Chem. Soc.* (*C*), 1968, 341; P. Lewis and G. H. Williams, *J. Chem. Soc.* (*B*), 1969, 120; J. M. Birchall, R. Hazard, R. N. Haszeldine, and W. W. Wakalski, *J. Chem. Soc.* (*C*), 1967, 47; J. P. B. Sandal, R. Bolton, and G. H. Williams, *J. Fluorine Chem.*, 1973—1974, **3**, 35.

[16] L. Benati, C. M. Camaggi, and G. Zanardi, *J.C.S. Perkin I*, 1972, 2817.

[17] M. Julia and B. Mallasine, *Tetrahedron Letters*, 1971, 987; J. G. Chottard and M. Julia, *ibid.*, p. 2561; *Tetrahedron*, 1972, **28**, 5615; S. Winstein, R. Heck, S. Lapporte, and R. Baird, *Experientia*, 1956, **12**, 138; D. H. Hey, G. H. Jones, and M. J. Perkins, *Chem. Comm.*, 1970, 1438; *J.C.S. Perkin I*, 1972, 105.

[18] H. Sakurai and A. Hosomi, *J. Amer. Chem. Soc.*, 1970, **92**, 7507.

[19] R. H. Thomson and A. G. Wylie, *J. Chem. Soc.* (*C*), 1966, 321.

[20] W. A. Boggust and W. Cocker, *J. Chem. Soc.*, 1949, 355.

[21] F. Taddei, P. E. Todesco, and P. Vivarelli, *Gazzetta*, 1965, **95**, 499.

[22] P. Bassignana, C. Cogrossi, and M. Gandino, *Chim. et Ind.* (*France*), 1963, **90**, 370 (*Chem. Abs.*, 1964, **60**, 4957).

[23] J. I. G. Cadogan and G. A. Molina, *J.C.S. Perkin I*, 1973, 541.

[24] G. P. Gardini, *Tetrahedron Letters*, 1972, 4113.

[25] T. Caronna, R. Galli, V. Malatesta, and F. Minisci. *J. Chem. Soc.* (*C*), 1971, 1747.

*Reactions of 2-Acylbenzothiazoles with Alkyl Radicals.*—With the exception of the dioxanylation of the 2-acetylbenzothiazole, which was effected under conditions identical to those reported in the literature for the parent compound,[26] all the other reactions were carried out according to the following general procedure. To a stirred solution of the 2-acylbenzothiazole (0.01 mol), the carboxylic acid (0.025 mol), and $AgNO_3$ (0.001 mol) in 5% $NH_3$ (35 ml) and MeCN (35 ml), heated at 90°, a solution of $(NH_4)_2S_2O_8$ (0.03 mol) in water (15 ml) was added dropwise over *ca.* 20 min. Stirring and heating was continued for 30 min and the cooled solution was then poured onto ice and $NH_3$; the mixture was extracted with chloroform and the organic layer was washed with 5% NaOH. From the combined aqueous solutions unchanged acid was recovered by acidification. The washed organic solution was dried and solvent was removed. The residue was chromatographed through a silica gel column using light petroleum (b.p. 40—60°)–ethyl ether (9 : 1) as eluant. The separation of the various components was monitored by g.l.c. and t.l.c. The compounds obtained are described in the Results and Discussion section. Yields of 2-alkylbenzothiazoles are reported in Table 1; those for the reactions of 5- and 6-substituted 2-acetylbenzothiazoles with Ad• were in the range of 50—60%. Simple alkylbenzothiazoles were already described in the literature; [7,22] physical, spectral, and analytical data of the 5- and 6-X-2-(1-adamantyl)-benzothiazoles are collected in Table 3.

1-Acetyladamantane was also obtained from the reaction carried out in the absence of acylbenzothiazoles; the yields, based on adamantane-1-carboxylic acid, were *ca.* 50%.

A solution of t-butyl adamantane-1-percarboxylate (0.25 g) and 2-acetylbenzothiazole (0.09 g) or 2-benzoylbenzothiazole (0.1 g) in acetonitrile (5 ml) was kept at 100°, in a sealed tube, for three days. Analysis by g.l.c. showed the presence of unchanged acylbenzothiazoles (30%) and 2-(1-adamantyl)benzothiazole (60% yield based on the reacted substrates).

*Competitive Experiments.*—(*a*) To an equimolecular mixture of a 5- or 6-X-2-acetylbenzothiazole and 2-acetylbenzothiazole (0.01 mol), adamantane-1-carboxylic acid (0.01 mol) and $AgNO_3$ (0.001 mol) in 5% $NH_3$ (35 ml) and MeCN (35 ml), heated at 90°, a solution of $(NH_4)_2S_2O_8$ (0.005 mol) in water (10 ml) was added in 1 ml portions. After each addition, samples were analysed by g.l.c. and the ratio of products formed determined; the values of the relative reactivities were obtained following the extrapolation procedure employed in the determination of the relative rates of alkylation of protonated pyridines.[3] The results collected in Table 2 are the average of at least two independent experiments; the experimental error was ±5%.

(*b*) The relative rates of 1-adamantylation were determined in the same way using equimolecular mixtures of benzothiazole and 5- or 6-X-benzothiazole. The average values are reported in Table 2.

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[26] W. Buratti, G. P. Gardini, F. Minisci, F. Bertini, R. Galli, and M. Perchinunno, *Tetrahedron*, 1971, **27**, 3655.