# Electrophilic Aromatic Reactivities *via* Pyrolysis of 1-Arylethyl Esters. Part 17.[1] The Reactivity of the 2- and 3-Positions of Benzo[*b*]furan and of All Positions in Benzo[*b*]thiophen

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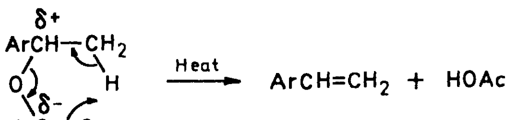
All six 1-(benzo[*b*]thienyl)ethyl acetates, 1-(benzo[*b*]furan-2-yl)ethyl acetate, and 1-(benzo[*b*]furan-3-yl)ethyl acetate have been prepared and their rates of gas-phase elimination of acetic acid measured between 620.2 and 686.7 K. The positional order of reactivity in benzo[*b*]thiophen is 3 > 2 > 6 > 5 > 4 > 7, which is both theoretically predicted, observed in solvolysis of 1-(benzo[*b*]thienyl)ethyl chlorides, and (in part) in electrophilic aromatic substitutions. The derived $\sigma^+$-values *viz.* −0.54, −0.39, −0.32, −0.29, −0.155, and +0.10 respectively, differ markedly for some positions from those obtained in the solvolysis, the values being more positive for all positions in the elimination. For benzo[*b*]furan the positional reactivity order is 3 > 2 in the elimination (the $\sigma^+$-values being −0.495 and −0.225, respectively) but changes to a 2 > 3 order in reactions possessing transition states closer in structure to that of the Wheland intermediate; this change in positional order with transition state structure is predicted by calculations. The data confirm that the extended selectivity relationship is a meaningless concept for parameterizing the reactivities of $\pi$-excessive heterocycles.

For each molecule the 3-position is more reactive, and the 2-position less reactive than the corresponding position in furan and thiophen. This order, the overall positional order in benzo[*b*]thiophen and the relative positional order in the benzenoid rings of benzo[*b*]thiophen, and dibenzothiophen are accounted for in terms of the structure of the most stable canonical form of the resonance hybrid representing the transition state.

IN 1962 one of us showed how the method of developing a carbocation in the $\alpha$-position of a side chain attached to an aromatic ring, the method introduced by H. C. Brown and his co-workers[2] for determining electrophilic aromatic substituent constants $\sigma^+$, could be applied to measuring the electrophilic reactivity of heterocycles.[3] We employed the reaction which has been the subject of this series of papers, namely the pyrolysis of 1-arylethyl acetates (1). This technique (involving different reactions) has since been applied by others to the determination of $\sigma^+$ values for heterocycles, in particular by Hill,[4] Noyce,[5] Topsom,[6] and Morgan[7] and their co-workers.



(1)

For benzene containing a very polarisable substituent such as MeO, no single substituent constant satisfactorily describes the aromatic reactivity at the *para*-position, so that the best quantitative treatment of reactivity data employs the Yukawa–Tsuno equation (1)[8] in which an extra parameter describes the extent of resonance interaction. For relatively non-polarisable substituents,

$$\log k/k_0 = \rho[\sigma + r(\sigma^+ - \sigma)] \qquad (1)$$

$\sigma^+ \approx \sigma$ so the value of $r$ is unimportant. It became apparent from our studies that application of the Hammett–Brown treatment to the $\pi$-excessive heterocycles furan and thiophen is not satisfactory especially in describing the reactivities of the 3-positions which appeared to be more polarisable than the 2-positions.[9,10] This application, the so-called 'extended selectivity relationship'[2] has nevertheless been applied to these molecules[11,12] with results which demonstrate the unsuitability of the technique. Thus the $\sigma^+$ values

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[1] Part 16, R. Taylor, *J.C.S. Perkin II*, 1978, 775.

[2] L. M. Stock and H. C. Brown, *Adv. Phys. Org. Chem.*, 1963, **1**, 35.

[3] R. Taylor, *J. Chem. Soc.*, 1962, 4881.

[4] E. A. Hill, M. L. Gross, M. Stasiewiez, and M. Mannion, *J. Amer. Chem. Soc.*, 1969, **91**, 7381.

[5] D. S. Noyce and D. A. Forsyth, *J. Org. Chem.*, 1974, **39**, 2828, and earlier papers in this series.

[6] T. J. Broxton, G. L. Butt, L. W. Deady, S. H. Toh, R. D. Topsom, A. Fischer, and N. W. Morgan, *Canad. J. Chem.*, 1973, **51**, 1620.

[7] G. T. Bruce, A. R. Cooksey, and K. J. Morgan, *J.C.S. Perkin II*, 1975, 551.

[8] Y. Yukawa and Y. Tsuno, *Bull. Chem. Soc. Japan*, 1959, **32**, 965.

[9] R. Taylor, *J. Chem. Soc. (B)*, 1970, 1365.

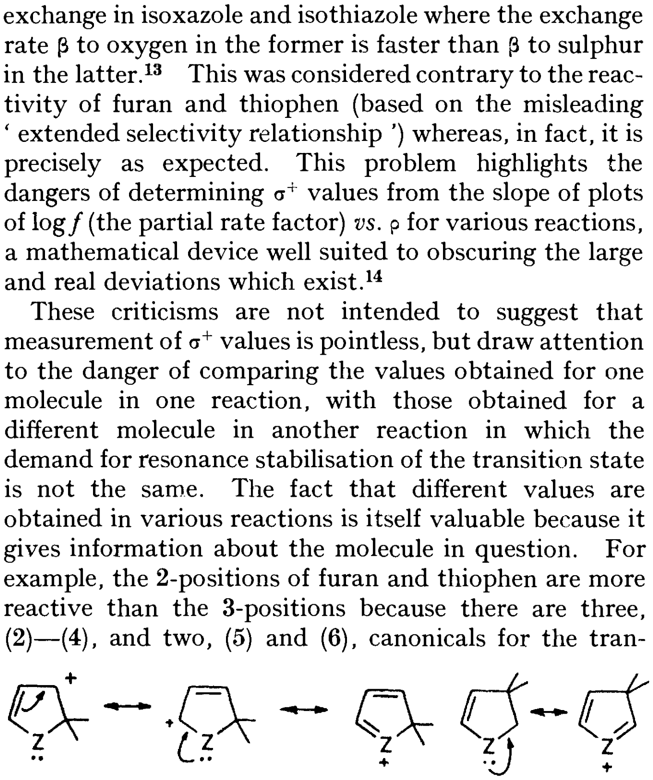
[10] R. Taylor, *J. Chem. Soc. (B)*, 1968, 1397.

[11] S. Clementi, P. Linda, and G. Marino, *Tetrahedron Letters*, 1970, 1389; *J. Chem. Soc. (B)*, 1970, 1153; S. Clementi and P. Linda, *Tetrahedron*, 1970, **26**, 2869.

[12] D. S. Noyce, C. A. Lipinski, and G. M. Loudon, *J. Org. Chem.*, 1970, **35**, 1718.

derived by this method are claimed to show that the 3-position of thiophen is more reactive than the 3-position in furan.[11] *Yet in no reaction is this true!* [4,7,9,10] The anomaly arises because the reactivity of furan has never been measured in reactions with high $\rho$-factors since these are carried out under highly acidic conditions in which furan decomposes. The reactivity of the more stable thiophen has, however, been measured in these reactions and since the $\sigma^+$ value derived from each reaction tends to increase with the reaction $\rho$-factor, it follows that the average $\sigma^+$ value (which the ' extended selectivity relationship ' in effect produces) is *larger* for thiophen than for furan. Use of this approach has led for example to some incorrect conclusions in hydrogen exchange in isoxazole and isothiazole where the exchange rate $\beta$ to oxygen in the former is faster than $\beta$ to sulphur in the latter.[13] This was considered contrary to the reactivity of furan and thiophen (based on the misleading ' extended selectivity relationship ') whereas, in fact, it is precisely as expected. This problem highlights the dangers of determining $\sigma^+$ values from the slope of plots of log $f$ (the partial rate factor) *vs.* $\rho$ for various reactions, a mathematical device well suited to obscuring the large and real deviations which exist.[14]

These criticisms are not intended to suggest that measurement of $\sigma^+$ values is pointless, but draw attention to the danger of comparing the values obtained for one molecule in one reaction, with those obtained for a different molecule in another reaction in which the demand for resonance stabilisation of the transition state is not the same. The fact that different values are obtained in various reactions is itself valuable because it gives information about the molecule in question. For example, the 2-positions of furan and thiophen are more reactive than the 3-positions because there are three, (2)—(4), and two, (5) and (6), canonicals for the transition states, respectively. The apparent greater polarisability of the 3- relative to the 2-positions [9] may then stem from the fact that half the structures for 3-substitution, but only a third of the structures for 2-substitution, involve the polarisable lone pair of electrons on sulphur.


(2) (3) (4) (5) (6)

The applicability of the ' extended selectivity relationship ' to benzo[*b*]thiophen has recently been considered [15] with the conclusion that it does not hold for reactions at the 2- and 3-positions (which is to be expected since the molecule consists of a polarizable benzo-substituent added to thiophen which is itself already polarizable), as described above. For the remaining positions, no analysis has hitherto been possible because data exist only for solvolysis of the 1-arylethyl chlorides.[5] We have therefore prepared, and measured the rates of pyrolysis of, the corresponding 1-arylethyl acetates.

In a previous analysis of reactivity data for the 2- and 3-positions,[16] one of us drew attention to the fact that 3-substitution is favoured in every reaction,[17,18] except isopropylation,[19] the products of which may be the result of rearrangement. (This has been made all the more probable by the fact that t-butylation of benzo[*b*]-thiophen has recently been shown to give mainly 3-substitution,[20] and 3-substitution in protic acid-catalysed t-butylation of benzo[*b*]furan becomes predominantly 2-substitution under flow conditions with Lewis acid catalysts.[21]) It has also been reported that in pyrolysis of 1-arylethyl acetates, the 2-position of benzo[*b*]thiophen was more reactive than the 3-position.[22] However, the following are features of this work. (i) Neither preparations nor physical properties for the compounds were reported (ii) The only rate cofficients quoted were those interpolated from Arrhenius data of indeterminate origin. (iii) Both the log ($A$/s$^{-1}$) values and the activation energies were abnormally low relative to these parameters for pyrolysis of 1-phenylethyl acetate. (iv) Surface-catalysed polymerisation of reaction products was taking place. (v) Rate data determined in the same study for furan and thiophen disagree not only with those which we had obtained earlier,[10] but the derived $\sigma^+$ values disagree with all other determinations. A re-evaluation of the reactivity of the 2- and 3-positions of benzo[*b*]thiophen in this reaction therefore seemed appropriate.

For benzo[*b*]furan the only quantitative reactivity data are for the 2- and 3-positions in solvolysis of 1-arylethyl acetates [4] and acetylation.[23] A measurement of the reactivity of the 2-position in pyrolysis of 1-arylethyl acetates has been reported,[22] but disagrees markedly with the other studies and is also subject to the same strictures noted above; in addition no Arrhenius data could be obtained because of surface reactions. We

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[13] S. Clementi, P. P. Forsythe, C. D. Johnson, A. R. Katritzky, and B. Terem, *J.C.S. Perkin II*, 1974, 399.

[14] R. Taylor, *Chem. Soc. Specialist Periodical Report*, 'Aromatic and Heteroaromatic Chemistry,' 1975, vol. 3, p. 220; R. Taylor, International Review of Science: ' Organic Chemistry, Series 2, 1976, vol. 3, p. 28.

[15] S. Clementi, P. Linda, and C. D. Johnson, *J.C.S. Perkin II*, 1973, 1250.

[16] R. Baker, C. Eaborn, and R. Taylor, *J.C.S. Perkin II*, 1972, 97.

[17] H. D. Hartough and S. L. Meisel, ' Heterocyclic Compounds. Compounds with Condensed Thiophene Rings,' Interscience, New York, 1954, pp. 4—10.

[18] B. Iddon and R. M. Scrowston, *Adv. Heterocyclic Chem.*, 1970, **11**, 244—245; M. H. Palmer, ' The Structure and Reactivity of Heterocyclic Compounds,' Arnold, London, 1967, pp. 319—320.

[19] S. F. Bedell, E. C. Spaeth, and J. M. Bobbitt, *J. Org. Chem.*, 1962, **27**, 2026.

[20] J. Cooper and R. M. Scrowston, *J.C.S. Perkin I*, 1972, 414.

[21] E. A. Karakhanov, G. V. Drovyannikova, L. A. Kisleva, and E. A. Viktorova, *Chem. Heterocyclic Compounds*, 1971, **7**, 956; B. L. Lebedev, N. A. Karev, O. A. Korytina, and N. I. Shuikin, *Bull. Acad. Sci. U.S.S.R.*, 1969, 2446.

[22] G. G. Smith and J. A. Kirby, *J. Heterocyclic Chem.*, 1971, **8**, 1101.

[23] Calculated from the data given by S. Clementi, P. Linda, and G. Marino, *J.C.S. Perkin II*, 1971, 79.

have, therefore, carried out a full study of the reactivities of the 2- and 3-positions of benzo[*b*]furan in the pyrolytic elimination.

## RESULTS AND DISCUSSION

The kinetic data are gathered in Table 1. These gave excellent Arrhenius plots, as indicated by the correlation coefficients (average 0.999 85) and we draw attention also to the fact that each ester gave a log ($A$/s$^{-1}$) value which was not only identical (well within the limits of experimental error) but identical also to that for 1-phenylethyl acetate. These two facts confirm the absence of surface reactions as do the reproducibility of the kinetic data. The activation energies given in the literature for those compounds which we have studied were also 3.3—4.7 kcal mol$^{-1}$ lower than we obtain confirming that the literature data were vitiated by the occurrence of a substantial amount of surface-catalysed elimination; they should, therefore, not be considered in evaluating the electrophilic reactivity of benzo[*b*]furan and benzo[*b*]thiophen.

TABLE 1

Pyrolysis of compounds $RCH(OAc)CH_3$

| R | $T$/°C | $10^3k$/s$^{-1}$ | log($A$/s$^{-1}$) | $E$/kcal mol$^{-1}$ | $\Delta S^{\ddagger}$ [a]/cal mol$^{-1}$ K$^{-1}$ | Corr. coeff. | log $k/k_0$ at 650 K |
|---|---|---|---|---|---|---|---|
| Phenyl [b] | | | 12.75 | 43.6 | −1.6 | | 0 |
| Benzo[*b*]furan-2-yl | 413.5 | 101 | 12.75 ± 0.33 [c] | 43.18 ± 1.01 [c] | −1.6 | 0.999 79 | 0.138 |
| | 405.3 | 71.3 | | | | | |
| | 393.0 | 40.0 | | | | | |
| | 388.4 | 29.9 | | | | | |
| | 380.3 | 20.4 | | | | | |
| | 372.6 | 13.7 | | | | | |
| | 371.0 | 12.8 | | | | | |
| Benzo[*b*]furan-3-yl | 410.6 | 127 | 12.58 ± 0.37 | 42.18 ± 1.12 | −2.7 | 0.999 65 | 0.302 |
| | 405.3 | 99.0 | | | | | |
| | 393.8 | 54.6 | | | | | |
| | 389.7 | 47.7 | | | | | |
| | 388.4 | 44.1 | | | | | |
| | 380.3 | 29.8 | | | | | |
| | 372.6 | 20.3 | | | | | |
| | 364.5 | 13.3 | | | | | |
| 2-Benzo[*b*]thienyl | 413.5 | 119.0 | 12.36 ± 0.28 | 41.7 ± 0.85 | −3.4 | 0.999 89 | 0.236 |
| | 405.2 | 83.0 | | | | | |
| | 396.6 | 56.8 | | | | | |
| | 389.7 | 40.8 | | | | | |
| | 371.0 | 15.7 | | | | | |
| | 353.0 | 6.31 | | | | | |
| 3-Benzo[*b*]thienyl | 413.5 | 156 | 12.79 ± 0.37 | 42.7 ± 1.13 | −1.4 | 0.999 82 | 0.329 |
| | 405.3 | 104 | | | | | |
| | 396.6 | 69.8 | | | | | |
| | 389.7 | 52.4 | | | | | |
| | 371.0 | 19.9 | | | | | |
| | 353.0 | 7.45 | | | | | |
| 4-Benzo[*b*]thienyl | 410.6 | 79.1 | 12.54 ± 0.18 | 42.68 ± 0.54 | −2.5 | 0.999 98 | 0.096 |
| | 405.2 | 62.5 | | | | | |
| | 389.7 | 29.4 | | | | | |
| | 372.6 | 12.4 | | | | | |
| | 354.6 | 4.85 | | | | | |
| 5-Benzo[*b*]thienyl | 410.6 | 94.4 | 12.52 ± 0.26 | 42.4 ± 0.77 | −2.6 | 0.999 95 | 0.137 |
| | 396.6 | 49.7 | | | | | |
| | 389.7 | 35.0 | | | | | |
| | 373.2 | 15.8 | | | | | |
| | 354.6 | 5.82 | | | | | |
| 6-Benzo[*b*]thienyl | 405.2 | 77.1 | 12.57 ± 0.35 | 42.5 ± 1.03 | −2.4 | 0.999 86 | 0.195 |
| | 396.6 | 51.0 | | | | | |
| | 389.7 | 37.2 | | | | | |
| | 373.2 | 16.7 | | | | | |
| | 354.6 | 6.01 | | | | | |
| 7-Benzo[*b*]thienyl | 413.9 | 64.5 | 12.64 ± 0.37 | 43.4 ± 1.12 | −2.1 | 0.999 83 | −0.063 |
| | 410.6 | 56.4 | | | | | |
| | 405.2 | 44.4 | | | | | |
| | 389.7 | 21.3 | | | | | |
| | 373.2 | 9.08 | | | | | |
| | 354.6 | 3.20 | | | | | |

[a] At 600 K. [b] Numerous rate data for this compound have been reported in previous parts of this series. [c] Errors in these columns are for 95% confidence limits.

From the log $k/k_0$ values at 650 K and the ρ-factor of —0.61 at this temperature, $\sigma^+$ values have been calculated and are given in Table 2 together with those determined in other reactions; they are also shown in Figure 1 along with those determined for furan and thiophen in acetate pyrolysis.[10] Notable features of the results are as follows. (i) The reactivity of the 3-position of benzo[*b*]furan is constant under all conditions whereas that of the 2-position is widely variable to the extent that it can be both more or less reactive than the 3-position depending upon the demand for resonance stabilisation of the transition state; this is predicted by molecular orbital calculations (see below). Moreover, the 2-position is less reactive than the 2-position in furan whereas the 3-position is more reactive than the 3-position in furan (but by a lesser amount). This can be understood in terms of the canonical forms (7) and (8) which are the principal contributors to the transition states for reaction at the 2- and 3-positions, respectively.[17] Structure (8) is benzenoid and, therefore, of low energy whereas structure (7) is not. Consequently resonance between the 2-position and the lone pair on oxygen is unfavourable and the inductive effect of oxygen will substantially lower the reactivity of the 2-position. However, there are overall more canonical forms for 2-substitution (and one is benzenoid) so that it is reasonable to expect that under conditions of higher resonance demand, the 2-position will become the more reactive.

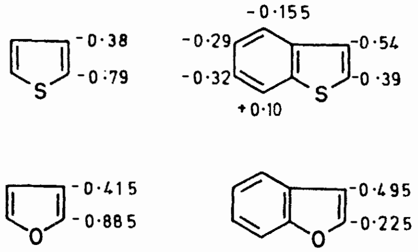
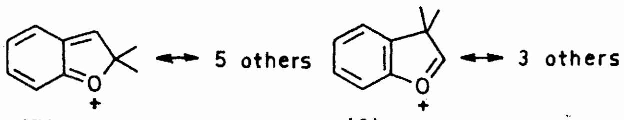


FIGURE 1 $\sigma^+$-Constants determined from pyrolysis of 1-arylethyl acetates

(ii) Whereas it may be possible to describe the reactivity of the 3-position of benzo[*b*]furan in terms of a $\sigma^+$ value of *ca.* $-0.48$, no such approach is possible for the 2-position.



(7) (8)

(iii) Since the 3-position of furan is more polarisable than the 3-position of benzo[*b*]furan whereas the 2-position of benzo[*b*]furan is more polarisable than the 2-position of furan, it follows that the relative reactivities of the corresponding positions will not remain constant, but can even invert so this should not be considered a discrepancy as indicated in the literature.[23]

(iv) The 3-position of benzo[*b*]thiophen is more reactive than the 2-position in acetate pyrolysis, as it is in all other reactions for which quantitative data are available (Table 2). The literature report of the reactivity of these positions in pyrolysis [22] is, therefore, confirmed as erroneous.

(v) In the reactions used to examine benzo[*b*]furan and also in solvolysis of the 1-arylethyl chlorides, benzo[*b*]thiophen shows similar features to those noted above under (i) *i.e.* the 2-position appears to be more polarisable than the 3-position, the reactivity of which can be described in these reactions by a $\sigma^+$ value of *ca.* $-0.55$. However, over the whole range of reactions in Table 2 a consistent reactivity pattern is less easy to distinguish and it is clear that the reactivity of neither position can be described by a single substituent constant. In contrast to the situation in benzo[*b*]furan, under no condition does the reactivity of the 2-position exceed that of the 3-position, because the $+M$ effect of sulphur is less than that of oxygen. (The $-I$ effect of sulphur is also smaller so that in the pyrolysis the 2-position of benzo[*b*]thiophen is more reactive than the 2-position in benzo[*b*]furan.)

TABLE 2

$\sigma^+$-Constants determined from various reactions

| | Benzo[*b*]thiophen | | | | | | Benzo[*b*]furan | | |
|---|---|---|---|---|---|---|---|---|---|
| Reaction | 2 | 3 | 4 | 5 | 6 | 7 | 2 | 3 | Ref. |
| Pyrolysis, 1-arylethyl acetates | $-0.39$ | $-0.54$ [a] | $-0.155$ | $-0.29$ | $-0.32$ | $+0.10$ | $-0.225$ [b] | $-0.495$ | This work |
| Solvolysis, 1-arylethyl chlorides | $-0.49$ | $-0.56$ | $-0.25$ | $-0.34$ | $-0.42$ | $-0.11$ | | | 5 |
| Solvolysis, 1-arylethyl acetates | $-0.43$ | $-0.52$ [a] | | | | | $-0.47$ [b] | $-0.46$ | 4 |
| Protiodesilylation | $-0.33$ | $-0.34$ | | | | | | | 24 |
| Positive bromination | $-0.39$ | $-0.69$ | | | | | | | 15 |
| Acetylation | $-0.49$ | $-0.58$ | | | | | $-0.575$ | $-0.48$ | 15 |
| Detritiation | $-0.61$ | $-0.62$ | | | | | | | 16 |
| Molecular chlorination | $-0.61$ | $-0.77$ | | | | | | | 15 |
| Molecular bromination | $-0.61$ | $-0.77$ | | | | | | | 15 |

[a, b] These data were obtained with the same ester, kindly provided by Professor E. A. Hill.

As in the case of benzo[*b*]furan relative to furan, the 2-position of benzo[*b*]thiophen is less reactive than the 2-position of thiophen whereas the 3-position is more reactive than the 3-position in thiophen (and also by a lesser amount) so the results are nicely consistent.

(vi) The positional reactivity order for benzo[*b*]thiophen is exactly the same as in solvolysis of 1-arylethyl chlorides, the same as estimated from qualitative electrophilic substitution patterns [25] and from calculations (see below). However there are marked discrepancies in some of the reactivities (up to 0.2 $\sigma^+$ units) so much so that for example the 7-position is deactivated in pyrolysis and activated in the solvolysis. Clearly

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[24] C. Eaborn and J. A. Sperry, *J. Chem. Soc.*, **1961**, 4921.

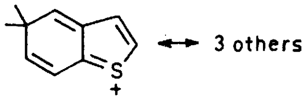
[25] O. Chalvet, R. Roger, and P. Demerseman, *Bull. Soc. chim. France*, **1970**, 1483.

the ' extended selectivity relationship ' cannot be applied to describing the reactivities of the positions in the benzenoid ring of benzo[*b*]thiophen either.

It is instructive to see how this reactivity order arises. In the transition states for reaction at the 2- and 3-positions some of the canonical forms are benzenoid for each position, whereas none are benzenoid in the transition states for reaction at the 4—7 positions. Consequently, the 2- and 3-positions will be the most reactive.

In the benzenoid ring the 5- and 6-position are the most reactive and this arises because for each position the canonical form in which the sulphur lone pair is delocalised to the reaction site in the transition state, is *p*-quinonoid, (9) and (10) respectively, and these structures are particularly stable.[26] Since there are more structures overall for 6-substitution, this position is the most reactive. For the 4- and 7-positions the canonical in which the sulphur lone pair is delocalised to the reaction site is *o*-quinonoid so these positions are the least reactive. Overall there are five structures for 4-substitution and four structures for 7-substitution so the observed reactivity pattern follows. It is interesting to note that the reactivity pattern in benzene[*b*]thiophen, substituted naphthalenes,[27] and isoquinoline [28] can all be explained in terms of these simple concepts.

Likewise we note that on going from benzo[*b*]thiophen to dibenzo[*b,d*]thiophen, the position *para* to sulphur becomes the most reactive.[29] Structures (11) and (12) show why. Structure (11) is more stable than (9) because it is benzenoid whereas (12) which corresponds to (10) is not and hence the relative reactivity order of these two β-positions inverts. Likewise annelation of the canonical for reaction at the 7-position produces a benzenoid structure whereas annelation of the canonical for reaction at the 4-position does not so the relative reactivities of these two positions becomes reversed in dibenzothiophen.



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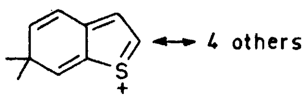

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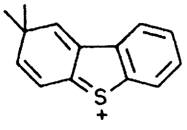

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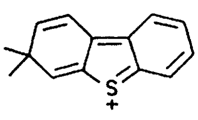

(12)

(vii) Though no data are available for reaction in the benzenoid ring of benzo[*b*]furan we predict that the 5-position will be the most reactive, and more reactive than the corresponding position in benzo[*b*]thiophen and also that there will be a greater reactivity difference between the 5- and 6-positions on the one hand, and the 7- and 4-positions on the other. This latter follows from the fact that the 4- and 7-positions are α to a strained ring whereas the 5- and 6-positions are β. The furan ring is more strained than the thiophen ring and the pattern predicted follows from relief of strain in the transition state under these circumstances.[30]

*Molecular Orbital Calculations*.—In previous determinations of the electrophilic aromatic reactivities of heterocycles [3,10,31] one of us showed these were best correlated in terms of π-electron densities calculated by the Hückel method.

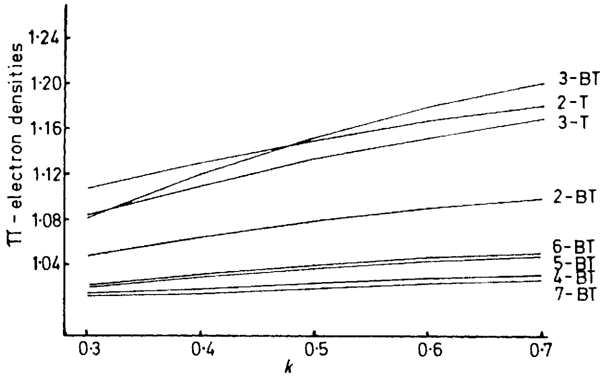

FIGURE 2 Variation of π-electron densities for thiophen (T) and benzo[b]thiophen (BT) with *k* values, for $h = 0$, $h' = 0$

For thiophen the data were reasonably correlated by the parameters $h(\alpha_S - \alpha_C/\beta) = 0$, $h'(\alpha_{C2,5} - \alpha_C/\beta) = 0$, $k(\beta_{CS}/\beta_{CC}) = 0.6$, these having been found earlier by Pilar and Morris to give a reasonable prediction of the reactivity of thiophen in other reactions.[32] We now find that π-electron density calculations are very successful for predicting the overall reactivity pattern in benzo[*b*]thiophen (BT) with values of $h = 0$, $h' = 0$, and $k$ ranging from $<0.3$ to $>0.7$ (Figure 2). This success is to be expected in view of the relatively small difference in electronegativity of carbon and sulphur so that the reactivity can be accounted for very simply in terms of the number and stability of the canonical forms for the transition state as noted above. Taken along with the data for thiophen (T) itself the correct reactivity order *viz*: 2T > 3BT > 2BT > 3T > 5BT > 6BT > 4BT > 7BT is not predicted by any of these values (Figure 2) since the 3-position of thiophen is predicted to be substantially more reactive than the 2-position of benzo[*b*]thiophen.

The results of a number of calculations of the reactivity of benzo[*b*]furan have been given in the literature.[25] SCF calculations of π-densities (two methods) and CNDO π-densities each gave the positional order 3 > 2 whereas SCF localisation energies gave the order 2 > 3, so Chalvet *et al.* considered the former results anomalous

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[26] H. G. Benson and J. N. Murrell, *J.C.S. Faraday II*, 1972, 129.

[27] C. Eaborn, P. Golborn, R. E. Spillett, and R. Taylor, *J. Chem. Soc.* (*B*), 1968, 1112.

[28] E. Glyde and R. Taylor, *J.C.S. Perkin II*, 1975, 1783.

[29] R. Baker and C. Eaborn, *J. Chem. Soc.*, 1961, 5077.

[30] R. Taylor, *J. Chem. Soc.* (*B*), 1968, 1559.

[31] R. Taylor, *J. Chem. Soc.* (*B*), 1971, 2382; *J.C.S. Perkin II*, 1975, 277; E. Glyde and R. Taylor, *ibid.*, p. 1783.

[32] F. L. Pilar and J. R. Morris, *J. Chem. Phys.*, 1961, **34**, 389.

since they believed that the correct reactivity order was $2 > 3$. However, in fact both these results are in excellent agreement with the reactivity pattern given in Table 2, for in reactions where the transition state is close to the ground state π-densities should govern the reactivity order *i.e.* $3 > 2$. By contrast where the transition state is closer in structure to the Wheland intermediate, then localisation energies are more appropriate indices, *i.e.* the order should be $2 > 3$.

In previous Hückel calculations of the reactivity of furan, one of us found that parameters of $h = 2.0$ or 1.9, $h' = 0.125$, and $k = 0.6$, or alternatively $h = 1.5$, $h' = 0.1$, and $k = 0.5$ gave reasonable π-densities. However for benzo[*b*]furan the former two sets are unsatisfactory but the latter are reasonable. From the change in π-densities with varying $k$ (Table 3) a value of $k$ of 0.58 is found to give an excellent correlation of the reactivities of the 2- and 3-positions of furan and benzo[*b*]furan (Figure 3). The parameters predict the overall positional reactivity for benzo[*b*]furan as $3 > 2 > 5 > 6 > 7 > 4$ whereas the SCF or CNDO π-densities predict a higher placing for the 7-position. We hope in due course to be able to avaluate the accuracy of these calculations.

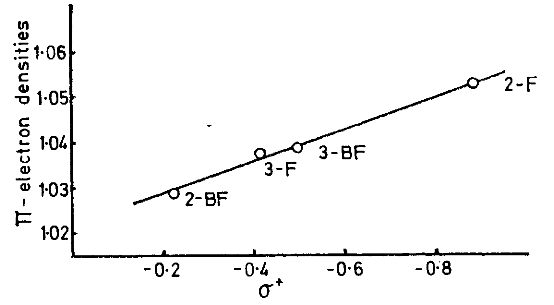

FIGURE 3 Correlation of reactivity of furan (F) and benzo[*b*]furan (BF) with π-electron densities

TABLE 3

π-Electron densities for furan and benzo[*b*]furan calculated for $h = 1.5$, $h' = 0.1$, and variable $k$

| $k$ | 2F | 3F | 2BF | 3BF |
|---|---|---|---|---|
| 0.5 | 1.048 | 1.022 | 1.033 | 1.0215 |
| 0.6 | 1.054 | 1.042 | 1.028 | 1.044 |
| 0.7 | 1.059 | 1.061 | 1.023 | 1.067 |

## EXPERIMENTAL

1-(*Benzofuran-2-yl*)*ethyl Acetate*.—This compound was very kindly donated by Professor E. A. Hill.

1-(*Benzofuran-3-yl*)*ethyl Acetate*.—1-(Benzofuran-3-yl)-ethyl alcohol was prepared as described in the literature [4] and acetylated with pyridine and acetic anhydride to give, after work-up, 1-(benzofuran-3-yl)ethyl acetate, b.p. 66—68 °C at 0.2 mmHg, $n_D^{20}$ 1.5286 (lit.,[4] b.p. 83 °C at 0.4 mmHg, $n_D^{25}$ 1.5330).

1-(2-*Benzo*[b]*thienyl*)*ethyl Acetate*.—1-(2-Benzo[*b*]thienyl)-ethyl alcohol was prepared by the literature method [4] and acetylated as above to give after work-up, 1-(2-benzo[*b*]-thienyl)ethyl acetate, b.p. 82—84 °C at 0.05 mmHg, m.p. 29—30 °C, $n_D^{25}$ 1.5768 (lit.,[4] 105 °C at 0.06 mmHg, m.p. 30—31 °C, $n_D^{22}$ 1.5755).

1-(3-*Benzo*[b]*thienyl*)*ethyl Acetate*.—This compound was very kindly donated by Professor E. A. Hill.

1-(4-*Benzo*[b]*thienyl*)*ethyl Acetate*.—1-(4-Benzo[*b*]thienyl)-ethyl alcohol was prepared by a literature method [5] and acetylated as above to give after work-up 1-(4-*benzo*[b]-*thienyl*)*ethyl acetate*, b.p. 66—68 °C at 0.03 mmHg, $n_D^{20}$ 1.5834 (Found: C, 65.2; H, 5.55. $C_{12}H_{12}SO_2$ requires C, 65.4; H, 5.5%), $\tau(CCl_4)$ 2.55 (5 H, m, ArH), 3.74 (q, $J$ 6.4 Hz, CH), 8.05 (s, $COCH_3$), and 8.43 (d, $J$ 6.4 Hz, $CH_3$).

1-(5-*Benzo*[b]*thienyl*)*ethyl Acetate*.—1-(5-Benzo[*b*]thienyl)-ethyl alcohol was prepared by a literature method [5] and acetylated as above to give after work-up, 1-(5-*benzo*[b]-*thienyl*)*ethyl acetate*, b.p. 96—98 °C at 0.04 mmHg, $n_D^{20}$ 1.5921 (Found: C, 65.4; H, 5.5%), $\tau(CCl_4)$ 2.54 (5 H, m, ArH), 3.75 (q, $J$ 6.4 Hz, CH), 8.06 (s, $COCH_3$), and 8.44 (d, $J$ 6.4 Hz, $CH_3$).

1-(6-*Benzo*[b]*thienyl*)*ethyl Acetate*.—1-(6-Benzo[*b*]thienyl)-ethyl alcohol was prepared by a literature method [5] and acetylated as above to give after work-up, 1-(6-*benzo*[b]-*thienyl*)*ethyl acetate*, b.p. 90—92 °C at 0.05 mmHg, $n_D^{20}$ 1.5027 (Found: C, 65.6; H, 5.55%), $\tau(CCl_4)$ 2.52 (5 H, m, ArH), 3.71 (q, $J$ 6.4 Hz, CH), 8.05 (s, $COCH_3$), and 8.45 (d, $J$ 6.4 Hz, $CH_3$).

1-(7-*Benzo*[b]*thienyl*)*ethyl Acetate*.—1-(7-Benzo[*b*]thienyl)-ethyl alcohol was prepared by a literature method [5] and acetylated as above to give after work-up, 1-(7-*benzo*[b]-*thienyl*)*ethyl acetate*, b.p. 60—62 °C at 0.02 mmHg, $n_D^{20}$ 1.5792 (Found: C, 65.8; H, 5.7%), $\tau(CCl_4)$ 2.61 (5 H, m, ArH), 3.91 (q, $J$ 6.4 Hz, CH), 8.04 (s, $COCH_3$), and 8.43 (d, $J$ 6.4 Hz, $CH_3$).

*Kinetic Studies*.—These were carried out in the general manner previously described.[10] The reactor was carefully preconditioned [33] with the products of pyrolysis of but-3-enoic acid at 420 °C (6 × 150 μl) before kinetic studies were carried out. Each ester gave excellent reproducible kinetics which were first-order to at least 95% of decomposition, and the rate coefficients obtained (Table 1), gave excellent Arrhenius plots with no deviations or curvature, confirming that no surface-catalysed elimination was taking place.

One of us (H. B. A.) thanks the University of Riyadh, Saudi Arabia, for a research scholarship.

[7/2198 *Received*, 16*th December*, 1977]

[33] R. Taylor, G. G. Smith, and W. H. Wetzel, *J. Amer. Chem. Soc.*, 1962, **84**, 4817.