

Aromatic Reactivity. Part L.¹ Thiophen, Benzo[*b*]thiophen, Anisole, and Thioanisole in Detritiation. Substituent Constants for Use in Electrophilic Aromatic Substitution

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Rates of detritiation in trifluoroacetic acid at various temperatures have been measured for [2-³H]- and [3-³H]-thiophen, [2-³H]- and [3-³H]-benzo[*b*]thiophen, [*p*-³H]anisole, and [*p*-³H]thioanisole. The approximate rates, *f*, relative to that for [³H]benzene at 70 °C, are 2.4×10^7 , 1.9×10^4 , 2.3×10^6 , 3.1×10^5 , 1.8×10^6 , and 7.0×10^4 , respectively, and aspects of these results are discussed. Hydrogen-bonding interaction between the methoxy-group and the trifluoroacetic acid results in about a 15-fold lowering of the rate constant for [*p*-³H]-anisole below the value which would be expected in the absence of such interaction.

In a plot of log *f* against σ^+ for the compounds studied, tritiated monosubstituted benzenes, and tritiated polynuclear aromatic hydrocarbons, the points mostly lie acceptably on a single straight line, but with a fairly large scatter. A set of σ^+ -constants, σ^+_{Ar} , which may be generally applicable to electrophilic aromatic substitution, has been derived from detritiation data for a large range of aromatic systems.

EARLIER Parts were concerned with detrimethylsilylation of trimethylsilyl derivatives of thiophen,² benzo[*b*]thiophen,³ anisole,⁴ and thioanisole,⁵ and we now describe the results of a study of the rates of detritiation of some of the monotritio-derivatives of these reactive aromatic compounds. Some of the results have been used previously.⁶⁻⁸ Since our work was completed, other workers have measured rates of protododeuteriation for furan and thiophen in H₂SO₄-H₂O-MeOH,⁹ and for the 4-position of anisole and thioanisole in H₂SO₄-AcOH,¹⁰ but the results are of limited value because the rates for few other aromatic compounds have been measured in these media. Rates of protododeuteriation for the 2- and 3-positions of thiophen have also been measured in trifluoroacetic acid at low temperatures.¹¹

RESULTS AND DISCUSSION

The first-order rate constants for detritiation of the compounds studied are shown in Table 1, along with approximate values, *f*, of the rates at 70 °C relative to that of [³H]benzene, these values, with one exception, being obtained by extrapolation of rate constants from lower temperatures. The extrapolations introduce some uncertainty into the values of *f*, but this is offset by the advantage that the values at 70 °C can be compared directly with those for a large range of other aromatic systems.

Some features of our results, and some comments, are as follows: (a) The 2-position of thiophen is *ca.* 1200 times as reactive as the 3-position. This is in satisfactory agreement with the factor of 3300 at 25 °C which can be derived from the work of Shatenshtein and his colleagues,¹¹ since a somewhat larger spread of rates would be expected at the lower temperature.

The value of the ratio log *f*₂ : log *f*₃, *viz.*, 1.73, is in good agreement with the corresponding ratio, *viz.*, 1.78, for desilylation.²

(b) Fusion with the benzene ring, to give benzo[*b*]thiophen, markedly lowers the reactivity at the 2-position by a factor of 10³ but raises the reactivity at the 3-position by a factor of 180, so that the 3- becomes a

TABLE I
Rates of detritiation in trifluoroacetic acid
10⁷k/s⁻¹

Compound	-10.0 °C	28.84 °C	40.00 °C	70 °C ^b	<i>f</i> ^a
[2- ³ H]Thiophen	2360	73,200		2.3 × 10 ⁶	2.4 × 10 ⁷
[3- ³ H]Thiophen				1.78 × 10 ³	1.9 × 10 ⁴
[2- ³ H]Benzothiophen		421	1810	2.2 × 10 ⁴	2.3 × 10 ⁵
[3- ³ H]Benzothiophen		600	2510	2.95 × 10 ⁴	3.1 × 10 ⁵
[<i>p</i> - ³ H]Anisole		270	1240	1.70 × 10 ⁴	1.8 × 10 ⁵
[<i>p</i> - ³ H]Thioanisole		124	538	6.7 × 10 ³	7.0 × 10 ⁴

^a Rate relative to that for [³H]benzene at 70 °C. ^b By extrapolation, except for [3-³H]thiophen.

little more reactive than the 2-position. In protodesilylation the reactivities of both the 2- and 3-positions are lowered by the fusion, but the effect is very much smaller for the 3- than for the 2-position, and again the 3- is slightly more reactive than the 2-position.³ Nitration, halogenation, chloromethylation, and mercuriation of benzothiophen all give predominantly the 3-isomer,¹² and acylation gives mainly 3-, but along with substantial amounts of 2-product in some cases.^{13,14} Anomalously,

⁹ K. Schwetlik, K. Unverferth, and R. Mayer, *Z. Chem.*, 1967, **7**, 58.

¹⁰ S. Oae, A. Ohno, and W. Tagaki, *Bull. Chem. Soc. Japan*, 1962, **35**, 681.

¹¹ E. N. Zvyagintseva, T. A. Yakushina, and A. I. Shatenshtein, *J. Gen. Chem. U.S.S.R.*, 1968, **38**, 1933.

¹² M. H. Palmer, 'The Structure and Reactions of Heterocyclic Compounds,' Arnold, London, 1967, pp. 319-320.

¹³ V. V. Ghaisas, *J. Org. Chem.*, 1957, **22**, 703.

¹⁴ S. Clementi, P. Linda, and G. Marino, *J. Chem. Soc. (B)*, 1971, 79.

¹ Part XLIX, K. C. C. Bancroft, R. W. Bott, and C. Eaborn, preceding paper.

² F. B. Deans and C. Eaborn, *J. Chem. Soc.*, 1959, 2299, 2303.

³ C. Eaborn and J. A. Sperry, *J. Chem. Soc.*, 1961, 4921.

⁴ C. Eaborn, *J. Chem. Soc.*, 1956, 4858.

⁵ C. Eaborn and P. M. Jackson, *J. Chem. Soc. (B)*, 1969, 21.

⁶ R. O. C. Norman and R. Taylor, 'Electrophilic Substitution in Benzenoid Compounds,' Elsevier, Amsterdam, 1965, p. 214.

⁷ R. Taylor, *J. Chem. Soc. (B)*, 1968, 1397.

⁸ R. Taylor, *J. Chem. Soc. (B)*, 1970, 1364.

isopropylation gives almost entirely 2-product,¹⁵ and it is possible that rearrangement to the thermodynamically most stable isomer follows the initial substitution in this case.

The value of the ratio $\log f_3 : \log f_2$ in detritiation, *viz.*, 1.02, is exactly the same as the corresponding ratio in protodetrimethylsilylation; the value of $\sigma_3^+ : \sigma_2^+$ where the σ^+ -values are derived from solvolysis of 1-arylethylacetates,¹⁶ has the slightly higher value of 1.10, but variations of this kind are quite normal. For example, in the case of thiophen the value of the ratio $\sigma_2^+ : \sigma_3^+$ itself varies from 2.08⁷ to 1.84¹⁶ to 1.70¹⁷ depending on the system used to derive the σ^+ -values, while the values of $\log f_2 : \log f_3$ for a range of reactions vary even more widely, between 2.08 and 1.54.⁷ Such variations can be reasonably attributed primarily to the differing balances of resonance and polar effects at the separate ring positions along with differing demands on the resonance effects in the several reactions.⁷

(c) Streitwieser and his colleagues have derived σ^+ -constants for various positions of polynuclear aromatic hydrocarbons from acetolysis of the arylmethyl tosylates.¹⁸ Examining a plot against σ^+ of values of $\log f$ for detritiation of tritiated polynuclear hydrocarbons in trifluoroacetic acid at 70 °C, they concluded that a straight line could not be drawn to pass between the points and the origin (benzene), and that the points lay on a smooth curve, suggesting that the polycyclic systems possibly cannot be treated in this context like monosubstituted benzenes.¹⁹ It is thus of interest to examine a plot of $\log f$ against σ^+ which includes not only the results for the polycyclic hydrocarbons and the values of σ^+ derived for such systems by Streitwieser *et al.*,¹⁸ but also those for some monosubstituted benzenes, and for the heterocyclic systems discussed above. The relevant data¹⁹⁻²⁷ are in Table 2, and the plot is shown in the Figure. Except for the very large deviation in respect of the 1-position of pyrene, the points in general lie acceptably well about a straight line ($\rho = -8.75$) drawn by inspection through the origin, though there is a rather large scatter. It seems to us that the single straight line through the origin is as satisfactory as, say, three separate straight lines for the polynuclear systems, the substituted benzenes, and the heterocyclic systems. In other words, σ^+ -constants apply to all three systems with a common value of ρ as well as they apply within any one system. The single straight line is also, except for the point for the 1-position of pyrene, as satisfactory as a smooth curve for the polynuclear systems, and we

¹⁵ S. F. Bedell, E. C. Spaeth, and J. M. Bobbitt, *J. Org. Chem.*, 1962, **27**, 2026.

¹⁶ E. A. Hill, M. L. Gross, M. Stasiewicz, and M. Manion, *J. Amer. Chem. Soc.*, 1969, **91**, 7381.

¹⁷ D. S. Noyce, C. A. Lipinski, and G. M. Loudon, *J. Org. Chem.*, 1970, **35**, 1718.

¹⁸ A. Streitwieser, jun., H. A. Hammond, R. H. Jagar, R. M. Williams, R. G. Jesaitis, C. J. Chang, and R. Wolf, *J. Amer. Chem. Soc.*, 1970, **92**, 5141.

¹⁹ A. Streitwieser, jun., A. Lewis, I. Schwager, R. W. Fish, and S. Labona, *J. Amer. Chem. Soc.*, 1970, **92**, 6525.

²⁰ K. C. C. Bancroft, R. W. Bott, and C. Eaborn, *J. Chem. Soc.*, 1964, 4806.

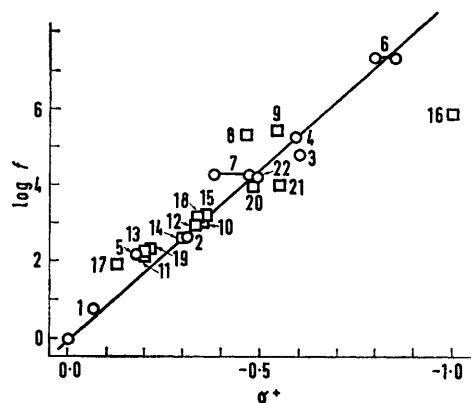
suggest that the deviation for this point is at least as likely to arise from an error in the value of σ^+ derived for the 1-position of pyrene by Streitwieser *et al.*¹⁸ as from

TABLE 2

Reactivities, f , relative to [³H]benzene for various compounds in detritiation in trifluoroacetic acid at 70 °C

No.	Compound	$\log f$	Ref.	$-\sigma^+$	Ref.
1	[<i>m</i> - ³ H]Toluene	0.78	20	0.066	25
2	[<i>p</i> - ³ H]Toluene	2.65	21	0.311	25
3	[<i>p</i> - ³ H]Thioanisole	4.84	Table 1	0.604	25
4	[<i>p</i> - ³ H]Anisole	5.25	Table 1	0.59 ^a	26
5	[4- ³ H]Biphenyl	2.21	35	0.179	27
6	[2- ³ H]Thiophen	7.38	Table 1	0.85, 0.80, 0.79	16, 17, 7
7	[3- ³ H]Thiophen	4.28	Table 1	0.49, 0.47, 0.38	16, 17, 7
8	[2- ³ H]Benzothiophen	5.36	Table 1	0.46	16
9	[3- ³ H]Benzothiophen	5.49	Table 1	0.54	16
10	[1- ³ H]Naphthalene	3.06	22	0.35	18
11	[2- ³ H]Naphthalene	2.18	22	0.20	19
12	[1- ³ H]Phenanthrene	2.96	1	0.33	19
13	[2- ³ H]Phenanthrene	2.24	1	0.20	19
14	[3- ³ H]Phenanthrene	2.59	1	0.30	19
15	[9- ³ H]Phenanthrene	3.21	1	0.36	19
16	[1- ³ H]Pyrene	5.91	19, 23	1.00	19
17	[2- ³ H]Pyrene	1.91	19, 23	0.13	19
18	[4- ³ H]Pyrene	3.15	19, 23	0.34	19
19	[2- ³ H]Triphenylene	2.23	19, 23	0.21	19
20	[3- ³ H]Fluoranthene	3.96	24	0.48	19
21	[6- ³ H]Chrysene	4.00	19, 23	0.55	19
22	[2- ³ H]Fluorene	4.23	20	0.49	27

^a Valid for trifluoroacetic acid solutions only



Plot of $\log f$ against σ^+ . Squares denote fused-ring compounds. Numbers denote compounds as in Table 2

a breakdown in the applicability of σ^+ -constants to polynuclear systems.

It thus becomes pertinent to note (a) that the σ^+ -constant for the 1-position of pyrene used by Streitwieser *et al.* was derived not from the acetolysis used to

²¹ R. Baker, C. Eaborn, and R. Taylor, *J. Chem. Soc.*, 1961, 4927.

²² C. Eaborn, P. Golborn, R. E. Spillett, and R. Taylor, *J. Chem. Soc. (B)*, 1968, 1112.

²³ A. Streitwieser, jun., P. C. Mowery, R. G. Jesaitis, and A. Lewis, *J. Amer. Chem. Soc.*, 1970, **92**, 6529.

²⁴ K. C. C. Bancroft and G. R. Howe, *J. Chem. Soc. (B)*, 1970, 1541; 1971, 400.

²⁵ L. M. Stock and H. C. Brown, *Adv. Phys. Org. Chem.*, 1963, **1**, 35.

²⁶ P. E. Peterson, D. M. Cherli, and K. A. Sipp, *J. Org. Chem.*, 1968, **33**, 972.

²⁷ H. C. Brown and T. Inukai, *J. Amer. Chem. Soc.*, 1961, **83**, 4825.

give the σ^+ -constants value for the other hydrocarbons, but indirectly from an arylmethyl chloride hydrolysis, and (b) that the σ^+ -constants obtained by Streitwieser *et al.* for the polynuclear hydrocarbons from the acetolysis depend on use of a value for ρ (*viz.*, -5.71) which is based on only three substituents, *viz.*, *p*-Me, *m*-Me, and *p*-F, for which the separate values of $\log f$ correspond to values of ρ of -5.46 to -5.66 , -6.52 , and -5.34 , respectively. It happens that values of σ^+ are available for 2-naphthyl (-0.135), 2-phenanthryl (-0.119), 3-phenanthryl (-0.196), and 2-anthracenyl (-0.295) which were derived either from the solvolysis used to define σ^+ -constants or from a closely related solvolysis,²⁷ and if these values are used in conjunction with the acetolysis rates recorded by Streitwieser *et al.*,¹⁸ they correspond with values of ρ of -8.18 , -9.67 , -8.67 , and -7.37 , respectively. The mean of the 7 separate ρ values is *ca.* -7.4 , and if this is used in place of the value of -5.71 adopted by Streitwieser *et al.*, the values of σ^+ derived from the acetolysis rates are smaller than those derived by the latter workers by a factor of $(7.4/5.7)$. If these revised values are used in the plot (not shown) against $\log f$, the overall scatter of points is somewhat reduced, and the deviation of the point for the 1-position of pyrene is only about 0.1 σ units, which is certainly less than the uncertainty in the value of σ^+ -constant in this case.

We must emphasize, however, that we regard straight-line plots of $\log f$ against σ^+ for the electrophilic aromatic substitutions as partly coincidental, since it seems clear to us that the balance of resonance and polar effects differs from reaction to reaction, and only by coincidence will it be the same for any other reaction as it is in the reaction used to define σ^+ . Plots of logarithms of relative rates against $[\sigma + r(\sigma^+ - \sigma)]$, which takes account of the differing balances of resonance and polar effects in different reactions are, in general, more satisfactory,²⁸⁻³¹ and it is fortuitous that for detritiation in trifluoroacetic acid the relevant value of r happens to be about unity, as it is, by definition, in the solvolysis used to define σ^+ -constants.^{25*} However, in the light of this coincidence, it seems appropriate to use the extensive range of data on relative rates in the detritiation to derive for a large number of aromatic compounds σ^+ -constants which may be applied approximately to other electrophilic aromatic substitutions; where necessary, of course, by use of the relationship $\log f = \rho[\sigma + r(\sigma^+ - \sigma)]$. Such values, based on a choice of -8.8 for the value of ρ in the detritiation, are shown in Table 3. Positions *ortho* to substituents have been omitted for substituted benzenes.

* We cannot, unfortunately, examine for the detritiation a plot of $\log f$ against $[\sigma + r(\sigma^+ - \sigma)]$ which includes data for the polycyclic and heterocyclic systems, because few of the relevant σ -constants are available.

²⁸ Y. Yukawa and T. Tsuno, *Bull. Chem. Soc. Japan*, 1959, **32**, 971.

²⁹ C. Eaborn and J. A. Waters, *J. Chem. Soc.*, 1961, 542; C. Eaborn and K. C. Pande, *ibid.*, p. 3715; R. W. Bott and C. Eaborn, *ibid.*, 1963, 2139.

³⁰ C. Eaborn and P. M. Jackson, *J. Chem. Soc. (B)*, 1969, 21.

³¹ Ref. 6, pp. 293-298.

TABLE 3

Values of σ_{Ar}^+ constants applicable to electrophilic aromatic substitutions

Aromatic compounds	Position of ³ H	$\log f$	Ref.	σ_{Ar}^+
Substituted benzenes				
Benzene	1	0.00		0.00
Toluene	4	2.65	21	-0.30
Toluene	3	0.78	20	-0.09
t-Butylbenzene	4	2.73	21	(-0.31) ^a
<i>o</i> -Xylene	4	3.28	32, 33	-0.37
Indane	5	3.61	33	-0.41
Tetralin	6	3.61	33	-0.41
Anisole	4	5.25	Table 1	(-0.60) ^{a,b}
Diphenylmethane	3	0.58	20	-0.07
Diphenylmethane	4	2.05	20	-0.23
Diphenyl ether	4	4.49	34	(-0.51) ^a
Diphenyl ether	3	<i>ca.</i> -0.93	34	(<i>ca.</i> +0.105) ^a
Diphenyl sulphide	4	3.995	34	-0.45
Thioanisole	4	4.84	Table 1	-0.55
Biphenyl	4	2.21	35	-0.24
4-Methylbiphenyl	4'	2.82	36	-0.32
4-Chlorobiphenyl	4'	1.68	36	-0.19
4-Bromobiphenyl	4'	1.62	36	-0.18
3-Chlorobiphenyl	4'	1.31	36	-0.15
Polycyclic compounds				
Biphenylene	1	2.02	37	-0.23
Biphenylene	2	4.15	37	-0.47
9,10-Dihydrophenanthrene	2	3.44	1	-0.39
Dihydroanthracene	1	2.65	32	-0.30
Dihydroanthracene	2	2.815	32	-0.32
Triptycene	1	1.71	32	-0.19
Triptycene	2	2.56	32	-0.29
Fluorene	2	4.23	20	-0.48
Fluorene	1	1.33	20	-0.15
Fluorene	3	2.10	20	-0.24
Fluorene	4	1.74	20	-0.20
9-Methylfluorene	2	4.24	38	-0.48
9,9-Dimethylfluorene	2	4.30	38	-0.49
2-Methylfluorene	7	4.81	36	-0.55
2-Chlorofluorene	7	4.65	36	-0.415
2-Bromofluorene	7	4.56	36	-0.40
Phenanthrene	1	2.96	1	-0.34
Phenanthrene	2	2.24	1	-0.25
Phenanthrene	3	2.59	1	-0.29
Phenanthrene	4	2.91	1	-0.33
Phenanthrene	9	3.21	1	-0.365
9-Fluorophenanthrene	10	3.93	39	-0.435
9-Fluorophenanthrene	1	2.09	39	-0.24
9-Chlorophenanthrene	10	2.48	39	-0.28
9-Bromophenanthrene	10	2.25	39	-0.26
9-Iodophenanthrene	10	2.36	39	-0.265
9-Methylphenanthrene	10	5.27	39	-0.62
Naphthalene	1	3.06	22	-0.35
Naphthalene	2	2.18	22	-0.25
2-Methylnaphthalene	1	5.56	22	-0.63
3-Methylnaphthalene	1	3.515	22	-0.40
4-Methylnaphthalene	1	4.97	22	-0.57
5-Methylnaphthalene	1	3.40	22	-0.39
6-Methylnaphthalene	1	3.18	22	-0.36
7-Methylnaphthalene	1	3.525	22	-0.40
8-Methylnaphthalene	1	3.25	22	-0.37
4-Phenylnaphthalene	1	4.27	22	-0.485
2-Fluoronaphthalene	1	3.30	22	-0.375
4-Fluoronaphthalene	1	3.73	22	-0.42
5-Fluoronaphthalene	1	1.70	22	-0.19
8-Fluoronaphthalene	1	1.79	22	-0.20
2-Chloronaphthalene	1	2.50	22	-0.28
3-Chloronaphthalene	1	0.43	22	-0.05
4-Chloronaphthalene	1	2.49	22	-0.28
5-Chloronaphthalene	1	1.52	22	-0.17
6-Chloronaphthalene	1	1.56	22	-0.18
7-Chloronaphthalene	1	2.21	22	-0.25
8-Chloronaphthalene	1	1.70	22	-0.19
2-Bromonaphthalene	1	2.28	22	-0.26
4-Bromonaphthalene	1	2.19	22	-0.25
5-Bromonaphthalene	1	1.47	22	-0.17

TABLE 3 (Continued)

Aromatic compounds	Position of ³ H	log <i>f</i>	Ref.	σ ⁺ _{Ar}
Polycyclic compounds				
8-Bromonaphthalene	1	1.73	22	-0.20
2-Iodonaphthalene	1	2.43	22	-0.28
4-Iodonaphthalene	1	ca. 2.32	22	ca. -0.26
8-Iodonaphthalene	1	2.88	22	-0.33
1-Methylnaphthalene	2	4.515	22	-0.52
3-Methylnaphthalene	2	2.21	22	-0.25
4-Methylnaphthalene	2	2.66	22	-0.30
5-Methylnaphthalene	2	2.43	22	-0.27
6-Methylnaphthalene	2	3.47	22	-0.39
7-Methylnaphthalene	2	2.38	22	-0.27
8-Methylnaphthalene	2	2.67	22	-0.30
1-Fluoronaphthalene	2	1.91	22	-0.22
3-Fluoronaphthalene	2	-0.19	22	+0.02
4-Fluoronaphthalene	2	-0.67	22	+0.08
1-Chloronaphthalene	2	1.05	22	-0.12
3-Chloronaphthalene	2	0.82	22	-0.09
4-Chloronaphthalene	2	0.185	22	-0.02
5-Chloronaphthalene	2	0.21	22	-0.02
6-Chloronaphthalene	2	1.44	22	-0.16
7-Chloronaphthalene	2	0.64	22	-0.07
8-Chloronaphthalene	2	0.49	22	-0.06
1-Bromonaphthalene	2	0.82	22	-0.09
3-Bromonaphthalene	2	0.65	22	-0.07
4-Bromonaphthalene	2	0.16	22	-0.01
8-Bromonaphthalene	2	0.31	22	-0.035
1-Iodonaphthalene	2	ca. 0.11	22	ca. -0.13
3-Iodonaphthalene	2	0.86	22	-0.10
4-Iodonaphthalene	2	0.47	22	-0.05
Fluoranthene	1	2.46	24	-0.28
Fluoranthene	2	1.85	24	-0.21
Fluoranthene	3	3.95	24	-0.45
Fluoranthene	7	2.40	24	-0.27
Fluoranthene	8	3.64	24	-0.41
3-Bromofluoroanthene	2	1.29	24	-0.15
4-Bromofluoroanthene	2	-1.15	24	+0.13
8-Bromofluoroanthene	2	1.53	24	-0.17
9-Bromofluoroanthene	2	1.44	24	-0.16
4-Bromofluoroanthene	3	2.96	24	-0.34
8-Bromofluoroanthene	3	3.57	24	-0.41
9-Bromofluoroanthene	3	2.96	24	-0.34
3-Bromofluoroanthene	8	3.14	24	-0.36
Chrysenes	6	4.00	19, 23	-0.45
Pyrene	1	5.91	19, 23	-0.67
Pyrene	2	1.91	19, 23	-0.22
Pyrene	4	3.15	19, 23	-0.36
Heterocyclic compounds				
Thiophen	2	7.38	Table 1	-0.84
Thiophen	3	4.28	Table 1	-0.49
Benzothiophen	2	5.36	Table 1	-0.61
Benzothiophen	3	5.49	Table 1	-0.62
Dibenzofuran	1	2.13	34	-0.24
Dibenzofuran	2	3.56	34	-0.40
Dibenzofuran	3	2.50	34	-0.28
Dibenzofuran	4	2.21	34	-0.25
Dibenzothiophen	1	2.44	34	-0.28
Dibenzothiophen	2	3.27	34	-0.37
Dibenzothiophen	3	2.64	34	-0.30
Dibenzothiophen	4	2.56	34	-0.29

^a Valid for trifluoroacetic acid solutions only. ^b Normal value, -0.78.

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³⁸ R. Baker, C. Eaborn, and J. A. Sperry, *J. Chem. Soc.*, 1962, 2382.

³⁹ C. Eaborn, A. Fischer, and D. R. Killpack, *J. Chem. Soc. (B)*, 1971, 2142.

(*d*) The value of -0.59 given for the σ⁺-constants of the *p*-OMe group is that suggested by Peterson and his colleagues for use in trifluoroacetic acid.²⁶ Use of the normal σ⁺ value -0.778 gives a point deviating badly from the line of the Figure, and from the deviation it can be calculated that the hydrogen-bonding interaction with the trifluoroacetic acid (see refs. 36, 40, 41) is responsible for about a 15-fold lowering of the reactivity at the *para*-position of anisole. Because of the effects of interaction with the acid, data for aromatic compounds containing alkoxy-, nitro-, and carboxy-groups have mostly been omitted from Table 3.

(*e*) In protodesilylation, a reaction of relatively low resonance demand (*r* = 0.65), the points for the 2- and 3-positions of benzothiophen show marked deviations from a plot of log *f* against σ⁺ in the opposite direction to those in the Figure, suggesting that the balance of resonance and polar effects is particularly variable in this heterocyclic system.

EXPERIMENTAL

[2-³H]- and [3-³H]-Thiophen.—(i) Thiophen was metalated with *n*-butyl-lithium in ether, and a molar proportion of tritiated water was cautiously added, followed by an excess of aqueous ammonium chloride. The ethereal layer was washed, dried (Na₂SO₄), and fractionated to give [2-³H]thiophen, b.p. 83°. (ii) Thiophen (10 g) was shaken vigorously with a mixture of concentrated sulphuric acid (4.2 ml) and tritiated water (1.8 ml, 180 mCi) for 27 h, at 25 °C (*cf.* ref. 42), and then recovered, dried (CaCl₂), and distilled. The product was shaken with concentrated (54%) perchloric acid (20 ml) for 19 h at 25 °C, and ether was added. Separation, washing, drying, and fractionation of the ethereal layer gave [3-³H]thiophen (6 g), b.p. 83 °C. Detritiation studies show that no significant quantity of the [2-³H]isomer was present.

[2-³H]- and [3-³H]-Benzo[*b*]thiophen.—(i) [2-³H]Benzo[*b*]thiophen, m.p. 32 °C, was prepared by a method used for [2-³H]thiophen, except that some tetrahydrofuran was used as well as ether as the solvent in the metallation. The product from distillation was recrystallized several times from ethanol. (ii) Bromination of benzothiophen in boiling carbon tetrachloride⁴³ gave 3-bromothiophen, b.p. 146–148° at 22 mmHg. The product (16 g, 0.083 mol) was converted into the Grignard reagent in ether by dibromoethane entrainment. Addition of tritiated water followed by the usual work-up, culminating in fractionation and recrystallization from ethanol, gave [3-³H]benzothiophen (7 g, 69%), m.p. 32 °C.

[*p*-³H]Anisole.—The Grignard reagent from *p*-bromoanisole in ether was treated with tritiated water, and the mixture worked up as usual to give [*p*-³H]anisole, b.p. 154 °C.

[*p*-³H]Thioanisole.—The Grignard reagent made from *p*-dibromobenzene and a 1-molar proportion of magnesium in ether at -30 °C was treated with tritiated water to give [*p*-³H]bromobenzene, b.p. 157 °C. This (12 g) was con-

⁴⁰ R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Anderson, and G. T. Davis, *J. Amer. Chem. Soc.*, 1963, **85**, 3146.

⁴¹ P. E. Peterson, *J. Org. Chem.*, 1966, **31**, 439.

⁴² K. Halvarson and L. Melander, *Arkiv Kemi*, 1955, 29.

⁴³ E. M. Crook and W. Davies, *J. Chem. Soc.*, 1937, 1697; G. Kommpa, *J. prakt. Chem.*, 1929, **122**, 319.

verted into the lithium derivative by treatment with lithium in ether, and thietan (5.9 g) was added with stirring during 30 min. The mixture was kept at room temperature for 20 h. Addition of aqueous ammonium chloride followed by the usual work-up gave [*p*-³H]thiophenol (5 g, 62%), b.p. 169 °C. This was methylated with dimethyl sulphate in aqueous sodium hydroxide to give [*p*-³H]thioanisole (3.0 g, 53%), b.p. 187–188 °C.

Rate Measurements.—The purification of the trifluoroacetic acid and the details of the rate measurements have been described.²¹ Good first-order kinetics were found in every case.

The rate of detritiation of [*p*-³H]toluene in the acid was effectively identical with that previously recorded,²¹ but

Streitwieser and his colleagues¹⁹ have obtained rates for [1-³H]- and [2-³H]-naphthalene which are some 20% lower than those we recorded²² in an acid which gave a rate for [*p*-³H]toluene identical with that obtained in the present work, but their values of the relative rates, *f*, agreed excellently with ours. Vaughan and Wright have recorded for [*p*-³H]toluene a rate 7% lower than ours.³³ We have also recently obtained rates for [*p*-³H]toluene lower than those we previously recorded, presumably as a consequence of some change in the quality of the acid commercially supplied. It is clear that the emphasis should be put on values of *f* in a batch of acid rather than on the absolute values of the rate constants.

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