SECTION B Physical Organic Chemistry

Measurement of Electrophilic Aromatic Reactivities via Pyrolysis of 1-Arylethyl Acetates. Part II.¹ The 2- and 3-Positions of Furan and Thiophen

By R. Taylor, School of Molecular Sciences, University of Sussex, Falmer, Brighton BNI 9QJ, Sussex

Rates of pyrolysis of 1-arylethyl acetates (where aryl = 3-furyl, 2-furyl, 2-thienyl, 3-thienyl, and phenyl) have been measured over a range of more than 50° for each compound between 311.3 and 379.1°. The relative rates of pyrolysis of the heterocyclic esters are found at 600°K to be: 2-furyl, 3.84; 2-thienyl, 3.31; 3-furyl, 1.88; 3thienyl, 1.785, which coupled with the previously determined ho-factor for the reaction leads to the corresponding σ^+ -values of -0.890, -0.795, -0.415, and -0.38. This is the first quantitative determination of the electrophilic reactivity of all four positions in one reaction and in the absence also of solvent, and shows the 3-position of furan to be slightly more reactive than that in thiophen, but the difference in reactivities between the 2- and 3-positions is greater in furan as indicated from qualitative work with reactions in solution. Comparison of the results with those obtained in electrophilic substitutions shows excellent agreement except in those reactions for which solvent effects have previously been postulated as important. Correlation of reactivity at the 3-position of thiophen is less good than that at the 2-position and indicates that the former is more susceptible to resonance and/or solvent effects.

Molecular orbital calculations show that for furan it is possible to correlate the σ^+ -values with those for pyridine (by means of either π -electron densities or localisation energies) by using reasonable parameters for the coulomb and resonance integrals, but for thiophen this approach fails completely indicating that the d-orbitals of sulphur play a significant role in determining the reactivity.

THE gas-phase pyrolysis of 1-arylethyl acetates proceeds via the partial formation of a carbonium ion on the carbon atom adjacent to the aromatic ring.² The electrondeficient centre is thus stabilised by electron supply from substituents in the ring just as they stabilise the transition states for electrophilic substitution.³ As evidence, the substituent effects correlate precisely with σ^+ -values in a Hammett plot, the p-factor for the reaction being -0.66 at 600° K. The reaction therefore provides an excellent model for electrophilic substitution with three outstanding advantages over all other reactions. First, the smallness of the p-factor means that relative rates can be measured *directly* and recourse to overlap techniques and extrapolations (with consequential opportunity for errors) is eliminated. Secondly, there is no solvent, so that doubts about the effect of solvation on modifying reaction rates are nonexistent. Thirdly, protonation of heteroatoms in heterocyclic molecules cannot occur so that the reaction is particularly suited to the determination of the reactivity of molecules for which the electrophilic reactivities have so far proved impossible to obtain in solution reactions because of this protonation. Thus in Part I¹ we presented the first determination of the electrophilic reactivity of the neutral pyridine molecule. Since then approximate values for the partial rate factor for nitration of the 3-position of neutral pyridine

¹ Part I, R. Taylor, J. Chem. Soc., 1962, 4881.

² R. Taylor, G. G. Smith, and W. H. Wetzel, J. Amer. Chem.

Soc., 1962, 84, 4817.
^a R. O. C. Norman and R. Taylor, 'Electrophilic Substitution in Benzenoid Compounds,' Elsevier, Amsterdam, 1965, p. 283.
⁴ C. D. Johnson, A. R. Katritzky, B. J. Ridgwell, and M.

Viney, J. Chem. Soc. (B), 1966, 1204. ⁶ R. D. Brown, A. S. Buchanan, and A. A. Humffray, Austral.

J. Chem., 1965, **18**, 1513.

has been published ⁴ as $\log k_3^{\text{Py}} : \log k^{\text{Ph}} \approx 2.3$ and 1.8and we note that our previously determined σ^+ -value predicts a value of $ca. 2 \cdot 1$ so that there seems good reason for supposing that the gas-phase reaction can be relied upon to predict results accurately for electrophilic substitutions.

The absence of solvent also means that the results obtained in the reaction can be used with some confidence for testing the validity of molecular orbital calculations. For pyridine we observed these calculations (using parameters which predicted the observed reactivities in other reactions) to be astonishingly successful (taken in isolation) in predicting the quantitative reactivities of the 2-, 3-, and 4-positions relative to benzene though the magnitude of the localisation energies appears to be too small if the scale of values obtained for polycyclic compounds can be regarded as meaningful. Thus for example the localisation energy for substitution in the β -position of naphthalene is predicted from the pyridine data to be -2.51 β instead of -2.48 β , the calculated value.

The electrophilic reactivities of furan and thiophen have attracted considerable attention particularly since there are inadequate data upon which to test molecular orbital calculations.⁵⁻¹¹ However, the reactivity of all four positions has never been worked out

- ¹⁰ S. Clementi, F. Gemel, and G. Marino, Chem. Comm., 1967, 498.
 - ¹¹ P. Linda and G. Marino, Chem. Comm., 1967, 499.

⁶ R. D. Brown, A. S. Buchanan, and A. A. Humffray, Austral. J. Chem., 1965, **18**, 1521. ⁷ R. D. Brown, A. S. Buchanan, and A. A. Humffray, Austral.

J. Chem., 1965, 18, 1527.

⁸ C. Eaborn, J. Chem. Soc., 1956, 4858; C. Eaborn and J. A. Sperry, J. Chem. Soc., 1961, 4921. 9

P. Linda and G. Marino, Tetrahedron, 1967, 23, 1739.

in one reaction, partly owing to the instability of furan (which for example renders detritiation impossible) and to the relative inaccessibility of the 3-derivatives. It therefore seemed appropriate to measure the rates of pyrolysis of the esters.

RESULTS AND DISCUSSION

The rates of pyrolysis of the esters at various temperatures are in Table 1 together with the values log

TABLE 1

Pyrolysis of compounds CH₃·CHR·OAc

				E		
		10^{3k}		(kcal./	ΔS^{\ddagger}	
R	Temp.	(sec.~1)	$\log A$	mole)	(e.u.)	$\log k/k_0$
Phenyl	376·3° 344·6 327·4	$11.5 \\ 1.91 \\ 0.667$	13.19	44.9	+0.4	0.0
	311.3	0.239				
3-Thienyl	379·0 371·5 356·0 340·7 327·1	$21.95 \\ 14.6 \\ 6.09 \\ 2.49 \\ 1.23$	12.92	4 3·5	-0.3	0.251
3-Furyl	$\begin{array}{c} 379 \cdot 1 \\ 371 \cdot 5 \\ 356 \cdot 0 \\ 340 \cdot 7 \\ 327 \cdot 1 \end{array}$	$24.0 \\ 15.65 \\ 6.40 \\ 2.74 \\ 1.275$	13.09	43 ·9	0.0	0.274
2-Thienyl	368.5 354.7 338.0 317.9	$21 \cdot 1 \\ 9 \cdot 53 \\ 4 \cdot 05 \\ 1 \cdot 30$	12.32	41.2	— 3 ∙5	0.524
2-Furyl	$368.5 \\ 355.1 \\ 344.7 \\ 337.9 \\ 317.9$	$23.4 \\ 11.75 \\ 6.70 \\ 4.44 \\ 1.52$	12.29	40.9	3.7	0.588

 k/k_0 (log $k_{\text{Het}}/k_{\text{Ph}}$), and the energies and entropies of activation, determined at 600° k by the least-mean-squares method. The error in determining E and ΔS^{\ddagger} are 0.1 kcal./mole and 0.2 e.u. for the phenyl ester and 0.6—0.9 kcal./mole and 0.9—1.4 e.u. for the heterocyclic esters.

The activation energy and rates of reaction of the phenyl ester are remarkably close to those which we previously obtained with a different reaction vessel¹ (the average rate difference is only 3%). (In Part I the temperature recorded for the phenyl ester as $322\cdot1^{\circ}$ should read $321\cdot2^{\circ}$. The activation energies for the phenyl and 3-pyridyl esters should read $44\cdot4$ and $44\cdot5$ kcal./mole, respectively; the other activation energies and the Arrhenius diagram are correct.) The variation in the entropy value is just outside the sum of the experimental errors and is probably not significant whereas the variation in the activation energy is clearly outside the sum of the experimental errors which accords with our previous observations that the reaction is controlled by variations in the activation energy.²

The Arrhenius diagram of the results is given in the Figure and the $\log k/k_0$ values are taken from this diagram at the point corresponding to 600° K. The σ^+ -values were obtained by dividing these values by the

J. Chem. Soc. (B), 1968

ρ-factor (-0.66 at 600° K). Statistical analysis was carried out to determine the deviation in the σ^+ -values at 600° K and the resulting absolute values (applying 50% confidence limits) are 2-furyl, -0.890 ± 0.016 ; 2-thienyl, -0.795 ± 0.020 ; 3-furyl, -0.415 ± 0.021 ; 3-thienyl -0.380 ± 0.024 . These values each include a contribution (± 0.009) due to possible error in the rate of the phenyl ester and it should be noted that in comparing the reactivity of one ester with another, this error should be *subtracted* from the possible errors in the absolute σ^+ -values. Hence all the ensuing comparisons are statistically meaningful.

The main features of the results are: (i) The 3-position of furan is slightly more reactive than the 3-position of



Arrhenius plots for the pyrolysis of 1-arylethyl acetates $Aryl = \bigoplus$ Phenyl, \bigcirc 3-thienyl, \triangle 3-furyl, \triangle 2-thienyl, \square 2-furyl

thiophen and this is the first evaluation of the relative reactivities of these positions. Both are considerably more reactive than the *para*-position in toluene ($\sigma^+ = -0.311$).

(ii) The 2-position of furan is more reactive than the 2-position of thiophen. This accords with the expectation from qualitative and quantitative electrophilic substitutions (see also later).

(iii) The difference in reactivity between the 2- and 3-positions is greater for furan than for thiophen. At first sight it may be thought that this is what one would have expected from qualitative observations in electrophilic substitutions, but this is not so for it can be easily shown that if $\sigma_2^+ - \sigma_3^+$ was constant for both furan and thiophen and $\sigma_{2-\text{furan}}^+$ was greater than $\sigma_{2-\text{thiophen}}^+$, then the ratio of 2-: 3-substitution would be greater in furan anyway. Hence the present result constitutes unambiguous evidence for the greater reactivity difference in furan than in thiophen.

(iv) The σ^+ -value for the 2-position of thiophen is slightly greater than that (-0.778) for the *para*-position in anisole and this is in excellent agreement with the

observations in protodesilylation 8 and acetylation 9 for which the former position is slightly the more reactive.

(v) Comparison of the present results with those obtained in electrophilic substitutions is illustrative and all the data so far available are gathered in Table 2.

First, it is clear that the results for protodemercuriation are wholly inconsistent with the other data and cannot be considered as meaningful, and Brown *et al.* concluded that this was so from consideration of the wide variation in the observed entropies of activation between the phenyl and heterocyclic isomers in that reaction.⁵ Likewise the results for protodeboronation seem erroneous and it has been pointed out that the differing tendencies of the boron atom to co-ordinate with able to respond to demands for resonance stabilisation of transition states, which is not unexpected. As a further indication of this, Marino *et al.*¹⁰ recently published relative reactivities of the 2-position of furan and thiophen in trifluoroacetylation which is a highly selective reaction (believed to be similar to molecular bromination, $\rho = -12 \cdot 1$). But to correlate their results with the σ^+ -values derived in this paper a ρ -value of about -20 is necessary. However, these results can be accommodated with a more reasonable ρ -value if it is assumed that the furan can respond more readily to demands for resonance than thiophen.

The above results show that the data for protodesilylation correlates most closely with that for pyrolysis. It would be interesting to have the result for

			TABLE 2				
Reaction	ę	$\log k_2$	$\log k_3$	σ_2^+	σ_3^+	$\frac{\log k_2}{\log k_3}$	Ref.
			Thiophen				
Pyrolysis	-0.66	0.520	0.251	-0.79	-0.38	2.08 + 0.12	a
Protodemercuriation	-2.87	3.23		-1.125			5
Protodesilylation	-4.6	3.683	2.061	-0.80	-0.45	1.78	8
Iododeboronation	-4.76	4.00	2.845	-0.84	-0.60	1.40	7
Protodeboronation	-4.94	5.93	3.85	-1.20	-0.78	1.54	6
Protodetritiation	-8.5	7.375	4.272	-0.87	-0.20	1.73	b
Molecular bromination	-12.1	9.708		-0.80			11
			Furan				
Pyrolysis	-0.66	0.584	0.273	-0.885	-0.415	2.14 + 0.12	a
Protodemercuriation	-2.87	3.602	2.176	-1.255	-0.76	$1\overline{\cdot 6}5$	5
Protodesilvlation	4.6	4.235		-0.92	aa		8
Molecular bromination	-12.1	11.785		-0.97			11
-	(T) 1 1		10 5 1	,			

^a This work. ^b R. Baker and C. Eaborn, personal communication.

water will differ in the isomers studied thereby making the results of little theoretical value. 6

The remaining results for thiophen show impressive consistency and it is clear that the pyrolysis provides an excellent model for studying electrophilic substitution effects in heterocyclic compounds. The reaction of the 2-positions are the most noticeably consistent and the fact that the pyrolysis results for the 3-position agree less well with the solution data is almost certainly related to the relatively poor correlation between the solution reactions themselves. It may, of course, be that substitution at the 3-position is particularly susceptible to demands for resonance stabilisation of the transition states, or it could be highly dependent upon solvation. It is, therefore, noteworthy that iododeboronation which has the least consistent results gave wide variation in the activation entropies for reaction of the phenyl and heterocyclic isomers and this was again attributed to variable solvation conditions.⁷ (It may well be that similar solvation effects are one of the reasons for the poor correlation of the rates of bromodeboronation with σ^+ -values.¹²)

For furan the agreement between the reactivities of the 2-position is again excellent. There is a slightly wider variation in the σ^+ -values than for the 2-position of thiophen and this points to furan being better

desilylation of the 3-position of furan and this investigation is in hand.

Molecular Orbital Calculations.—Previously ¹ we found that the σ^+ -values for pyridine correlated excellently with π -electron densities if the parameters $h(\alpha_{\rm N}-\alpha_{\rm C}/\beta) =$ 0.5, $h'(\alpha_{\rm C2}-\alpha_{\rm C}/\beta) = 0.085$ and $k(\beta_{\rm CN}/_{\rm CC}\beta) = 1.0$ were used, these values having been indicated as appropriate from work on quinoline ¹³ and isoquinoline.¹⁴ Densities of 0.957, 0.982, and 0.951 for the 2-, 3-, and 4-positions were obtained respectively. For a linear correlation of σ^+ with π -electron densities for pyridine, furan, and thiophen, the densities of 1.021 and 1.044 are predicted for the 3- and 2-positions of thiophen respectively, and 1.023 and 1.050 for the 3- and 2-positions of furan respectively.

Three closely similar sets of parameters were found to give the π -electron densities for furan which were required. These were h = 2.0, h' = 0.125, k = 0.6 (1.048, 1.020) h = 1.9, h' = 0.125, k = 0.6 (1.050, 1.022), and h = 1.5, h' = 0.1, k = 0.5 (1.048, 1.022) and any of these sets of parameters seems fairly reasonable for oxygen, the latter being perhaps rather less so.

¹² Ref. 3, pp. 255-258.

¹³ R. D. Brown and R. D. Harcourt, *J. Chem. Soc.*, 1959, 3451.

¹⁴ R. D. Brown and R. D. Harcourt, Tetrahedron, 1960, 8, 23.

However, for thiophen, h (and hence h') are both clearly =ca. 0 and a value of 0.6 has been suggested ¹⁵ as reasonable for k, but this leads to densities of 1.168 and 1.152at the 2- and 3-position respectively and these do not correlate at all with the predicted data.

Analysis of localisation energies is also not very encouraging. For pyridine an excellent correlation was obtained with h = 0.5, h' = 0.085, k = 1.0, and h'modified at the localised 2-position by the factor δ where $\delta = 0.43$, this value having also been indicated by earlier work.^{14} Extrapolation of the plot of σ^+ against β for pyridine leads to predicted values for the localisation energies of the 3- and 2-positions of thiophen of -2.465 and -2.39 respectively, and of the 3- and 2-positions of furan of -2.46 and -2.37, but these values are inconsistent with a comparison of the reactivity of the 5-membered heterocyclic with polycyclic compounds which lead to values of approximately -2.385, -2.22, -2.37, and -2.18, severally. This indicates that correlation of polycyclic and heterocyclic reactivities with localisation energies on the same scale is not feasible or that correlation of reactivities of π -excessive and π -deficient heterocycles with localisation energies on the same scale is not feasible. We have attempted to find which parameters would fit the predicted reactivities from both sets of data indicated above and analysis of the variables showed that the localisation energies for furan which correlate quantitatively with those for pyridine can be obtained by using the parameters h = 2.0, h' = 0.3, k = 1.1, and $\delta = 0.65$, whilst those values which quantitatively correspond to localisation energies of polycycles can be obtained from $h = 2.0, h' = 0.2, k = 1.2, \text{ and } \delta = 0.23$. For thiophen no correlation is possible whatsoever. As Pilar and Morris showed, using the reasonable values for sulphur of h and h' = 0, and k = 0.6, localisation energies of -1.696 and -2.052 are obtained for the 2- and 3-positions respectively. Increasing k causes the values to approach each other so that, at k = 1.0, both positions have the same value of -2.000. Clearly, no calculation which does not take the *d*-orbitals of sulphur into account will be successful, as was indicated by Longuet-Higgins.16

We plan to examine the relevance of these parameters to other heterocyclic systems in this reaction. We note that a very recent S.C.F.-M.O. treatment of thiophen claims that the calculated reactivities of the 2- and 3-positions agree well with the experimental reactivities.¹⁷ Qualitatively there is agreement in that both positions are predicted to be more reactive than benzene, the former being the most reactive. Quantitatively,

18 H. D. Hartough and A. I. Kosak, J. Amer. Chem. Soc., 1946, 68, 2639.

- D. I. Duveen and J. Kenyon, J. Chem. Soc., 1936, 621.
 M. Bellenghi, G. Carrara, F. Fava, E. Ginoulhiac,
- С. Martinuzzi, A. Vechi, and G. Weitnauer, Gazzetta, 1952, 82, 773. ²¹ Ya. L. Goldfarb and M. B. Ibraginova, Dokaldy Akad.
- Nauk S.S.S.R., 1957, 113, 594.

however, the agreement is poor as the 3-position is predicted to be very much less reactive than the 2-position and close in reactivity to benzene.

EXPERIMENTAL

1-Phenylethyl Acetate.-This was obtained in 92.5% overall yield (based on acetophenone) by the method previously described ² [b.p. 73°/4 mm. (lit.,² 105-108°/ 15 mm.)].

1-(2-Furyl)ethyl Acetate.-2-Acetylfuran was prepared in 43% yield from furan, acetic anhydride, and hydrogen iodide by the method of Hartough and Kosak,18 and had b.p. 86°/21 mm. (lit.,¹⁸ 45-48/5 mm.). 2-Acetylfuran was reduced to 1-(2-furyl)ethyl alcohol by the borohydride method, and the crude alcohol acetylated with pyridine and acetic anhydride at room temperature during 2 days. Work up yielded 1-(2-furyl)ethyl acetate (52% based on ketone), b.p. 72°/15 mm., $n_{\rm p}^{20}$, 1·4575 (lit., ¹⁹ 85/18 mm., $n_{\rm p}^{15}$, 1·4618 (Found: C, 62·3; H, 6·5. Calc. for C₈H₁₀O₃: C, 62.2; H, 6.5%). The refractive indices differ somewhat but the literature sample gave a very high carbon-hydrogen analysis (the calculated values 19 being also considerably in error) and it seems certain that this sample was contaminated with alcohol since this has both a higher refractive index 19 and carbon-hydrogen content.

1-(2-Thienyl)ethyl acetate.-Reduction of 2-acetylthiophen (Koch-Light Ltd.) by the borohydride method gave 1-(2-thienyl)ethyl alcohol (77%), b.p. 94°/18 mm., $n_{\rm p}^{20}$, 1.5476. Acetylation of the alcohol with acetic anhydride and pyridine gave 1-(2-thienyl)ethyl acetate (72%), b.p. 67°/3 mm. (lit.,20 78-81°/4 mm.; lit.,21 115-117°/16 mm., $n_{\rm D}^{20}$, 1.5054 (lit.,²¹ 1.5088) (Found: C, 56.1; H, 5.9. Calc. for $C_9H_{10}O_2S$: C, 56.4; H, 5.9%). The literature value of the refractive index also suggests alcohol contamination.

1-(3-Furyl)ethyl acetate.---Many and persistent attempts to prepare 3-furoic acid by the method of Gilman and Burtner ²² starting with coumalic acid obtained from malic acid ²³ failed to give yields and m.p.s quoted and this route cannot be recommended. The acid was prepared in 24%overall yield from ethyl sodio-oxalate (Koch-Light Ltd.) by the routes of Sutter,²⁴ Reichstein, et al.²⁵ and Sherman and Amstutz.26 This yield could be increased if flame heating was used for decarboxylation since frothing was difficult to control with electric heating (Sherman and Amstutz recommend a metal bath but this seems less desirable). 3-Furoic acid was converted into 3-furoyl chloride by the method of Gilman and Burtner ²² in 68%yield, b.p. 84°/85 mm., m.p. 29° (lit., 22 29°). The literature 22 b.p. of $65^{\circ}/47$ mm. does not correspond with that obtained in this work. 3-Furoyl chloride was converted into pure white crystals of 3-acetylfuran (87%), b.p. $96^{\circ}/70$ mm., m.p. 49.5-50.5° (lit.,27 51.5-52°) by the method given

22 H. Gilman and R. R. Burtner, J. Amer. Chem. Soc., 1933,

55, 2903. ²³ R. H. Wiley and N. R. Smith, Org. Synth., Coll. Vol. IV, Wiley, New York, 1963, p. 201.

- H. Sutter, Annalen, 1932, 499, 47.
- ²⁵ T. Reichstein, A. Grossner, K. Schindler, and E. Hardmeier, Helv. Chim. Acta, 1933, 16, 276.
- ²⁶ E. Sherman and E. D. Amstutz, J. Amer. Chem. Soc., 1950, 72, 2195. ²⁷ K. Naya, Nippon Kagaku Zosshi, 1956, 77, 759 (Chem. Abs.,
- 1958, 52, 348i).

F. L. Pilar and J. R. Morris, J. Chem. Phys., 1961, 34, 389.
 H. C. Longuet-Higgins, Trans. Faraday Soc., 1949, 45, 173.
 D. T. Clark, Tetrahedron, 1968, 24, 2567.

for *o*-nitroacetophenone.²⁸ Reduction of 3-acetylfuran by the borohydride method followed by acetylation of the crude alcohol with pyridine and acetic anhyride gave 1-(3-furyl)ethyl acetate (70% based on ketone), b.p. $72^{\circ}/14$ mm., n_{D}^{20} 1.4539 (Found: C, 61.8; H, 6.5%). Gas chromatographic analysis showed this compound to be at least 99% pure.

1-(3-Thienyl)ethyl acetate.--3-Bromothiophen (Aldrich Chemical Co.) (25 g., 0.155 mole) was treated with 1.5Mn-butyl-lithium (100 ml.) in hexane at -80° during 2 hr.²⁹ and then with acetaldehyde (7 g., 0.16 mole). Work-up and acetylation of the crude alcohol with acetic anhydride in pyridine gave 1-(3-thienyl)ethyl acetate (7.7 g., 30% based on the bromo-compound) b.p. $76^{\circ}/3$ mm., $n_{\rm D}^{20} =$ 1.5067 (Found: C, 56.7; H, 5.8%).

Apparatus.—The apparatus 30,31 was redesigned with the following improvements: The reaction vessel was constructed from Firth Vickers Staybrite F.M.B. Stainless Steel (equivalent to American I.S.I. Type 316) which has greater resistance to hot acetic acid and greater hardness (important in view of the metal-to-metal valve seats employed) than the American I.S.I. Type 304 previously used. The silver-soldered joints in the original apparatus were difficult to make gas-tight initially and inevitably leaked after a period at high temperature. They were therefore eliminated either by machining parts from a single piece of steel or by electron-beam welding of the joints. The copper gasket (described incorrectly as 'Everdur' in the original publication ³⁰) was crushed between knife edges machined into the steel mating pieces; this give a much more reliable seal. Viton rubber O-rings were used instead of neoprene because of the improved stability to high temperature. The valve handles were constructed with spokes to speed shut down after injection, and the injection septem was fitted with a Perspex dome with a hole in the centre (through which the hypodermic needle passed) and a nitrogen feed through the side. Thus any possible leakage on injection through the silicon rubber septum would be of nitrogen gas, which would not affect the vessel surface.

The hypodermic syringe was a Hamilton's gas-tight type (Teflon plunger) modified by having a rigid nylon cap fitted (with Araldite) to the upper end through which nitrogen could be passed. Thus any gas which leaked past the plunger into the vessel would be nitrogen. The hypodermic needle was fitted with a Hamilton's Kel-F hub to refuce the possibility of leakage between needle hub and syringe.

Manometers were fitted with Teflon needle valves at

their upper end. Absolute evacuation was easily achieved by forcing the mercury under pressure up past the open valve and then closing down. Release of the pressure gave a high vacuum which was retained for many weeks. Any subsequent outgassing of the mercury could be dealt with by repeating the procedure. All connections in the gas line were restricted to flexible metal couplings with neoprene O-rings or short lengths of neoprene tubing (which has excellent low-gas-diffusion properties). The balancing gas was 99.995% argon and the ballast was only 2.5 litres; this proved advantageous over the previous 20 l. ballast system for which adiabatic cooling of the gas released from the supply cylinder proved troublesome during the initial part of fast runs.

The furnace was controlled by an A.E.I. Resistance Thermometer Controller Type RT3R which gave very much greater temperature stability (0.1° during any day and often between days) and the desired temperature could be prechosen to within 0.3° or better.

Method of Pyrolysis .- The general method has been described.³¹ The rate of pyrolysis of each ester was determined from single runs carried out at a minimum of four different temperatures and over a temperature range of not less than 50°. The reaction vessel surface was conditioned initially by carrying out a number of runs with the 2-furyl ester and leaving the products for a number of hours in the vessel. This was more satisfactory than but-3-enoic acid ³¹ in eliminating surface reactions for these esters which were markedly sensitive to surface effects and gave zero-order plots and polymerisation (indicated by a pressure decrease after P_{∞} for the elimination) when the surface was still active. Thus runs which were not linear of the first order to at least 90% of the observed reaction were not included, and in favourable cases linearity to 98% was obtained. Preliminary runs showed that rate constants could be reproduced to $\pm 3\%$ for the heterocyclic esters and $\pm 2\%$ for the phenyl ester.

Molecular orbital calculations were performed on the University I.C.T. 1905 computer.

I thank Mr. M. D. Wood of the Chemical Laboratory Workshops and Mr. R. Lower of Appleby and Ireland Ltd., Reading, for help in constructing and improving the reaction vessel, particularly with regard to electron-beam welding, and Mr. C. Silk for the computer programme. I thank the S.E. Gas Board for a gallon of crude coal tar base (used in the decarboxylation of furantetracarboxylic acid).

[8/463 Received, March 29th, 1968]

```
30 G. G. Smith and F. D. Bagley, Rev. Sci. Instr., 1961, 32,
```

^{703.} ³¹ G. G. Smith, F. D. Bagley, and R. Taylor, J. Amer. Chem. Soc., 1961, 83, 3647.

²⁸ G. A. Reynolds and C. R. Hauser, Org. Synth., Coll. Vol. IV, Wiley, New York, 1963, p. 708. ²⁹ S. Gronowitz and H. O. Karlsson, Arkiv. Kemi, 1960, 17, 89.