801. *The Kinetics of Anionotropic Rearrangement. Part X.* A Comparison of the Effects of the Phenyl, Furyl, and Thienyl Groups on Reactivity.*

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The acid-catalysed rearrangements of the substituted allyl alcohols X·CH(OH)·CH:CHMe ⟶ X·CH:CH·CH(OH)Me, where X = 2-furyl and 2-thienyl, in aqueous dioxan have been studied kinetically. The results provide the first quantitative data on the effects of the five-membered heterocyclic systems on side-chain reactivity and are compared with those previously obtained with X = phenyl and *p*-methoxyphenyl. Under identical conditions, the furyl and thienyl derivatives rearrange, respectively, about 40 and 100 times faster than the phenyl analogue and with energies of activation about 3 kcal./mole lower. The mobility of the furyl derivative is very similar to that of the *p*-methoxyphenyl derivative.

The results are discussed in relation to other chemical and physical evidence concerning the electronic influence of oxygen and sulphur atoms.

ALTHOUGH the " aromatic " properties of five-membered heterocyclic compounds, such as furan and thiophen, have been much discussed, there are few quantitative data relating to the reactivity of such systems and their derivatives. In previous papers in this series, it was demonstrated that the acid-catalysed rearrangement of substituted allyl alcohols provides a very suitable basis for quantitative studies of the effects of complex or unstable groups on reactivity and we have now applied this method to a comparison of the influence of the phenyl, furyl, and thienyl groups. As previously, the systems used are the 1-substituted 3-methylallyl alcohols, the syntheses and rearrangements of which have been described in the preceding paper.

Kinetic data for the 2′-furyl and 2′-thienyl derivatives, and for the phenyl and *p*-methoxyphenyl analogues, are summarised in Tables 1 and 2. Under the conditions employed,

TABLE 1. *First-order rate-constants* (10^4k *min.*$^{-1}$) *for the rearrangements* X·CH(OH)·CH:CHMe ⟶ X·CH:CH·CHMe·OH *in aqueous dioxan*–0·001M-*hydrochloric acid* (c_s = *dioxan concentration in vol.* %).

	X = 2-Furyl		X = 2-Thienyl	
	c_s = 60%	80%	60%	80%
0°	99	(35) *	39	(13) *
30	1,660	780	640	290
40	3,990	2,070	1,760	850
50	10,400	5,500	4,950	2380
60	21,000	11,100	10,100	5400

* Solid dioxan tends to crystallise in the medium.

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* Part IX, *J.*, 1950, 800.

TABLE 2. *Relative rate constants* (*r*), *Arrhenius energies of activation* (*kcal./mole*) *and probability factors* ($k/c_A = Ae^{-E_{Arr.}/RT}$, where c_A = acid concentrations in mole./l).

	60% Aqueous dioxan			80% Aqueous dioxan		
X	*r* (at 30°)	$E_{Arr.}$	log *A*	*r* (at 30°)	$E_{Arr.}$	log *A*
Phenyl[1]	1	19·5	13·3	1	21·6	14·8
2-Furyl	90	16·2	12·2	114	18·3	13·3
2-Thienyl	35	16·5	12·0	43	19·0	13·5
p-Methoxyphenyl[2]	105	17·9	14·1	—	—	—

[1] *J.*, 1946, 396; 1948, 1982. [2] *J.*, 1947, 1096.

the rearrangements of the heterocyclic derivatives exhibit straightforward first-order kinetics and go to over 98% completion. As observed in other cases (cf. *J.*, 1948, 1982; 1950, 800), the reactions are slower and have higher energies of activation in 80% than in 60% aqueous dioxan. In 60% aqueous dioxan at 30°, the 2-furyl derivative reacts 90 times faster than the phenyl analogue and nearly as fast as the *p*-methoxyphenyl analogue. The 2-thienyl derivative reacts about 35 times faster than the phenyl analogue. [The rate ratios are somewhat dependent on the solvent and are slightly larger in 80% aqueous dioxan, indicating that the solvent effect is in part a primary solvation effect dependent on the substituent, as has been noted previously (*J.*, 1947, 1096).] Table 2 shows that the faster rates of rearrangement of the heterocyclic derivatives compared with the phenyl analogue are due to a lowering of about 3 kcal./mole in the energies of activation, partly offset by a simultaneous decrease in the non-exponential factor of the Arrhenius expression.

DISCUSSION

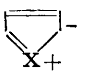
It is well known that thiophen undergoes electrophilic substitution more readily, and furan still more readily, than benzene, but apart from the present results for the anionotropic rearrangements the only quantitative information concerning the relative reactivities of phenyl, furyl, and thienyl derivatives appears to come from Catlin's data (*Iowa State Coll. J. Sci.*, 1935, **10**, 65) for the dissociation constants of furoic and thenoic acid, and from Kindler's data (*Ber.*, 1936, **69**, 2792) for the alkaline hydrolysis of the corresponding ethyl esters. These are collected in Table 3, together with data for the corresponding *p*-methoxyphenyl and *p*-methylthiophenyl derivatives for comparison. Three facts are immediately apparent. First, the furyl and thienyl groups increase reactivity relatively to phenyl in *all* the reactions (neglecting the slight anomaly of the rather dubious value for ethyl thenoate). Secondly, in anionotropy an oxygen atom attached to a phenyl ring has an accelerating effect very similar to that of a hetero-oxygen atom, but in dissociation and alkaline hydrolysis, oxygen and sulphur atoms attached to a phenyl ring have retarding effects opposite to those of the heterocyclic groups. Thirdly, the effects due to an oxygen atom are always larger than those due to a bivalent sulphur atom, independently of the structural type and of whether the influence is accelerative or decelerative; this is also in agreement with the qualitative evidence concerning direct electrophilic substitution of furan and thiophen.

TABLE 3. *Effects of oxygen- and sulphur-containing substituents.*

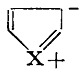
X	X·CH(OH)·CH:CHMe[1]	$X \cdot CO_2H$[2]	$X \cdot CO_2Et$[3]
Phenyl	1·00	6·3	1·00
2-Furyl	90	75	5·3
2-Thienyl	35	34	(0·9)[4]
p-Methoxyphenyl	105	3·4	0·22
p-Methylthiophenyl-	—	6·1	0·70

[1] Relative rates of acid-catalysed anionotropic rearrangement in 60% aqueous dioxan at 30° (this paper; *J.*, 1947, 1096). [2] Dissociation constants (10^5K) in water (Dippy, *Chem. Reviews*, 1939, **25**, 151; Catlin, *loc. cit.*; Bordwell and Cooper, *J. Amer. Chem. Soc.*, 1952, **74**, 1058). The value for *p*-methylthiobenzoic acid is extrapolated from data for 50% aqueous ethanol. [3] Relative rates of alkaline hydrolysis in aqueous ethanol at 30° (Kindler, *loc. cit.*) or aqueous acetone at 25° (Tommila and Hinshelwood, *J.*, 1938, 1801; Price and Hydock, *J. Amer. Chem. Soc.*, 1952, **74**, 1943). [4] This value appears very doubtful, as the rate constants show >50% drift in the single run quoted.

Furyl and thienyl groups may be expected to exert two opposing electronic influences. There will be an electron-withdrawing inductive (−*I*) effect, caused by the electronegativities of the hetero-atoms; independently of the basis of computation, the values increase in the sequence H$<$ C $<$ S $<$ O (Pauling, "Nature of the Chemical Bond," Cornell Univ. Press, 1940; Coulson, "Valence," Oxford Univ. Press, 1952) and thus $-I_{\text{Phenyl}} < -I_{\text{Thienyl}} < -I_{\text{Furyl}}$. Secondly, there will be an electron-donating mesomeric ($+M$) effect due to the ability of the hetero-atoms to share their unshared *p*-electron pairs. This mesomeric polarisation can be expressed in terms of contributions from resonance structures such as (I) and (II), which have been estimated by Schomaker and Pauling (*J. Amer. Chem. Soc.*, 1939, **61**, 1769) to be of the order of 15% in furan and 20% in thiophen on the basis of bond-length and dipole-moment data; thus, $\pm M_{\text{Phenyl}} < +M_{\text{Furyl}} \sim M_{\text{Thienyl}}$. Actually the quantitative significance of Schomaker and Pauling's analysis is somewhat uncertain because it neglects the "hybridisation moment" of the hetero-atom (Longuet-Higgins, *Trans. Faraday Soc.*, 1949, **45**, 173); moreover, in the case of thiophen, bond lengths indicate a greater contribution of structures containing S=C bonds than dipole moments. To account for the discrepancy, Schomaker and Pauling postulated some contribution from structures (III) and (IV) of reversed polarity, in which the sulphur valency shell is expanded to a decet of electrons. The participation of the 3*d*-orbitals of sulphur in the hybridisation of the π-electrons of thiophen has been supported by molecular-orbital calculations (Longuet-Higgins, *loc. cit.*) and will decrease the electron-donating properties



(I)



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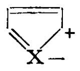
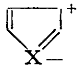


(III)

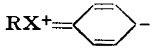


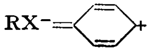
(IV)

of the thienyl group; in the terminology of substituent effects, the mesomeric effect of thienyl should be described as $\pm M$, with $+M$ predominating. The additional inductomeric (I') and electromeric (E) effects, representing changes in polarisability which can facilitate the attainment of the transition state in a reaction, will have the same sign as the permanent I and M effects operating in the ground state. Thus, we may have $+E_{\text{Furyl}}$, but $\pm E_{\text{Thienyl}}$ effects.

The influence of the heterocyclic systems may be expected to be paralleled by groups such as methoxyphenyl and methylthiophenyl relative to phenyl. The $-I$ effects will be similar, while the $\pm M$, $\pm E$ effects are represented by contributions from structures such as (V) and (VI). In fact the mesomeric moments of PhOMe and PhSMe calculated

(V)





(VI)

from recorded values (*Trans. Faraday Soc.*, 1934, **30**, Appendix) are approximately 0·07 and 0·13 D and the relation $+M_{\text{O}} \sim +M_{\text{S}}$ is also indicated by the dipole effects of oxygen and sulphur substituents in other unsaturated systems (Hannay and Smyth, *J. Amer. Chem. Soc.*, 1946, **68**, 1005; cf. below).

It is well established that acid-catalysed anionotropy is facilitated by electron-donating substituents, the first step being reversible addition of a proton to the migrating group (cf. Braude, *Quart. Reviews*, 1950, **4**, 404), and the data in Table 3 show that electron-accession increases in the sequence phenyl $<$ thienyl $<$ furyl $\sim$ *p*-methoxyphenyl. Clearly, in this reaction the combined $+M$ and $+E$ effects outweigh the $-I$ effects and since it has been deduced that $-I_{\text{S}} < -I_{\text{O}}$, and $+M_{\text{O}} \sim +M_{\text{S}}$, it follows that $+E_{\text{S}} < +E_{\text{O}}$, *i.e.*, that the electromeric polarisability of the thienyl group is *less* than that of the furyl and the methoxyphenyl group. The conclusion that $+E_{\text{S}} < +E_{\text{O}}$ is in agreement with Bennett and Hafez's data (*J.*, 1941, 652; cf. Baddeley, *J.*, 1950, 663) on the reaction of *p*-substituted phenylethyl alcohols $R\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot OH$ with hydrobromic acid; here also the first step is the addition of a proton to the hydroxyl group and the rates increase in the sequence R $=$ H $<$ SMe $<$ OMe. Thus, the sequence of positive electromeric effects due to O and S is the same, whether the atoms are incorporated in a heterocyclic ring or attached to a phenyl group, and equal to the sequence of mesomeric effects. An increase in mesomeric and electromeric interaction with increasing atomic size is expected from polarisability considerations (cf. Ingold, *Chem. Reviews*, 1934, **15**, 225) and from energy considerations of orbital overlap (Mulliken, *J. Amer. Chem. Soc.*, 1950, **72**, 4493); on the other hand, steric considerations of orbital overlap lead to the opposite prediction because the ratio of the electron-shell radius to bond length is less favourable with large atoms (cf. Baddeley, *J.*, 1950, 663). The only other periodic group for which reliable information is available is the halogens; here $+M$ effects decrease with atomic size (Braude and Stern, *J.*, 1947, 1096; Baker and Hopkins, *J.*, 1949, 1089, and earlier references there cited), while the predominant portion of the polarisability effects appears to be inductomeric rather than electromeric (Baker and Hopkins, *loc. cit.*). It is interesting that the relation $+E_S < +E_O$ is the reverse of that predicted by spectral analogies, since the auxochromic properties of SR are much larger than those of OR substituents (Bowden and Braude, *J.*, 1952, 1068).

We now turn to the data for carboxylic acid dissociation and for alkaline hydrolysis of ethyl carboxylic esters. Unlike anionotropy, these reactions are facilitated by electron-withdrawal from the reaction centre but the furyl and thienyl groups again have an activating influence relative to phenyl. This is surprising since the effects of groups usually become reversed in processes of opposite electronic requirements, giving rise, for instance, to an inverse relation between rates of anionotropy and acid dissociation constants (cf. *J.*, 1947, 1096). Moreover, *p*-methoxyphenyl and *p*-methylthiophenyl groups, unlike the heterocyclic groups, do, in fact, have a deactivating influence on the carboxyl reactions in contrast to their influence on anionotropy. In the carboxyl reactions, no $+E$ effects will be brought into play, but $-I$ effects will be reinforced by inductomeric $-I'$ effects and possibly, in the case of sulphur derivatives, by $-E$ effects involving *d*-orbitals. In the case of the OMe and SMe substituents, the data show that the $+M$ effects outweigh even the combined $-I$, $-I'$, and any $-E_S$ effects, thus leading to overall electron accession hindering the reaction, and that $+(-I, +M, -E)_{\mathrm{SMe}} < +(-I, +M)_{\mathrm{OMe}}$. This is a plausible result in so far as the mesomeric effects will be transmitted more powerfully than the inductive effects across the phenyl ring and will be enhanced by the carboxyl group, while the inductomeric effects are relatively weak (cf. Ingold, *J.*, 1933, 1120); the $-E_S$ effect, if it contributes at all, must evidently be quite weak also.

The unexpected activating influence of the heterocyclic groups on the carboxyl reactions are less easily explained. The data indicate that, in this case, the combined $-I$ and $-I'$ effects outweigh the $+M$ effects, thus leading to overall electron-recession facilitating the reaction, and that here $-(-I, +M)_{\mathrm{Thienyl}} < -(-I, +M)_{\mathrm{Furyl}}$ (the signs in front of the bracket are not used algebraically, but to signify that the overall effects are negative, *i.e.*, electron-attractive). It is not readily apparent why the relative magnitudes of the $-I$ and $+M$ effects should be reversed in the heterocyclic groups, nor can the difficulties be solved by recourse to a $-E$ effect involving the expansion of valency shell of the sulphur atom to a decet of electrons in the transition state, since if this were large it would make the total electron-attractive influence of the thienyl group larger than that of the furyl group. The most reasonable explanation seems to be that the $+M$ effects are considerably smaller for the heterocyclic groups than for the *p*-methoxyphenyl and methylthiophenyl groups relatively to phenyl, *i.e.*, that the permanent resonance interaction between the heterocylic and the CO_2R group is smaller than that between the aryl and the CO_2R group. This deduction is open to experimental test, but the required data are not at present available.

EXPERIMENTAL

The kinetic measurements were carried out by the technique previously described (Braude and Fawcett, *J.*, 1950, 800), the rates of rearrangement being determined by following the changes in ultra-violet light absorption intensity at the wave-lengths at which the rearranged isomers exhibit their characteristic maxima. The alcohols were those described in the preceding paper. The final absorption curves and intensities in solution agreed within experimental error with those of the rearranged isomers determined separately, showing that, under the conditions chosen, the rearrangements went to over 98% completion and were not accompanied by dehydration or other side-reactions. (The absolute values of the wave-length and intensities of the maxima differ slightly from those given in the preceding paper which were determined on a Hilger photographic instrument; in the present work, a Beckman photoelectric instrument

Rearrangements of 1-2′-*furyl*-3-*methylallyl alcohol.*

(i) In 0·001M-hydrochloric acid, 60% (by vol.) dioxan–water at 30°. Alcohol concn. 0·0044 mole/l.

Time (min.) ...	0	2	3	4	6	8	60	
$E^{1\%}_{1\,\text{cm.}}$ (2640 Å) ...	24	395	543	657	854	993	1342	
10^4k (min.$^{-1}$) ...	—	1660	1670	1640	1660	1650	—	(Mean) 1660

(ii) In 0·001M-hydrochloric acid, 80% (by vol.) dioxan–water at 30°. Alcohol concn. 0·0048 mole/l.

Time (min.) ...	0	4	6	8	10	12	80	
$E^{1\%}_{1\,\text{cm.}}$ (2640 Å)	24	383	510	649	760	834	1368	
10^4k (min.$^{-1}$) ...	—	785	750	782	790	767	—	(Mean) 775

(iii) In 0·001M-hydrochloric acid, 60% (by vol.) dioxan–water at 50°. Alcohol concn. 0·0049 mole/l.

Time (sec.)	0	25	47	68	87	105	127	1200	
$E^{1\%}_{1\,\text{cm.}}$ (2640 Å)	24	473	750	930	1038	1115	1165	1320	
10^4k (min.$^{-1}$) ...	—	10,200	10,500	10,600	10,500	10,300	10,800	—	(Mean) 10,500

Rearrangements of 3-*methyl*-1-2′-*thienylallyl alcohol.*

(i) In 0·001M-hydrochloric acid, 60% (by vol.) dioxan–water at 30°. Alcohol concn. 0·0061 mole/l.

Time (min.)	0	3	6	9	12	15	180	
$E^{1\%}_{1\,\text{cm.}}$ (2780 Å) ...	100	241	362	465	543	612	930	
10^4k (min.$^{-1}$) ...	—	644	630	637	633	638	—	(Mean) 636

(ii) In 0·001M-hydrochloric acid, 80% (by vol.) dioxan–water at 30°. Alcohol concn. 0·0056 mole/l.

Time (min.)	0	15	20	25	30	35	240	
$E^{1\%}_{1\,\text{cm.}}$ (2780 Å) ...	26	350	422	489	546	595	923	
10^4k (min.$^{-1}$)	—	296	291	290	289	288	—	(Mean) 291

(iii) In 0·001M-hydrochloric acid, 60% (by vol.) dioxan–water at 50°. Alcohol concn. 0·0060 mole/l.

Time (sec.)	0	18	37	52	67	82	540	
$E^{1\%}_{1\,\text{cm.}}$ (2780 Å) ...	26	244	411	527	605	667	875	
10^4k (min.$^{-1}$)	—	9900	9800	10,200	10,500	10,300	—	(Mean) 10,100

was employed.) The plots of the logarithms of the rate-constants at different temperatures against $1/T$ were satisfactorily linear. Six typical runs are reproduced above; in several cases the values of k differ slightly from those given in Table 1 which were averaged from duplicate runs.

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