The Isoimide–Imide Rearrangement

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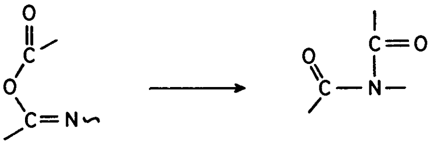
When imidoyl chlorides (8) are solvolysed in the pH range 3—13 in aqueous dioxan in the presence of acetate or benzoate ions, the isoimides (10) are formed *in situ*. These isoimides undergo acid (pH <4.5) and base (pH >11.5) catalysed acyl transfer to the solvent, giving the amides (12). But at intermediate pH (6—11) rearrangement to the *N*-acyl form (11) (the Mumm rearrangement) alone occurs. The specific rate of this O ⟶ N acyl group migration is pH independent and shows a low solvent effect (*m* 0.175). Substituents attached to carbon or nitrogen have the same effect (ρ −0.84). When the migrating group R is varied a non-linear Hammett plot is observed, with ρ +0.60 for electron-withdrawing and +1.65 for electron-donating substituents. The changeover point is a function of the migrating terminus varying from R = Ph (when Y = H) to R = *p*-tolyl (when Y = *p*-NO_2). Rate-determining O ⟶ N acyl transfer is suggested in all cases, but this is preceded by an equilibrium which favours the *Z* form (10a) when R is electron donating.

SINCE the discovery of the Mumm[1a] rearrangement [(1) ⟶ (2)] attempts have been made to study it in many systems.[1b] The *O*-acyl materials (1) have been proposed as intermediates in several reactions, *e.g.* peptide synthesis,[2,3] but until recently only in cyclic systems[4,5] such as (3) where the nucleophilic imino-nitrogen is restrained from attacking the isoimide carbonyl group (because of steric restrictions), could *O*-acyl materials be isolated as stable compounds. The first acyclic *O*-acylisoamides isolated were the *N*-(2,4-dinitrophenyl)benzimidoyl benzoates (4) of Curtin and Miller,[6] but attempts to prepare analogous materials which did not contain the dinitrophenyl group were unsuccessful. Subsequently relatively stable *O*-acyl compounds have been found in two other systems (5)[7] and (6).[8] The materials were formed initially in the *Z* form and this was confirmed by n.m.r. and *X*-ray data. Schwarz[9] has also studied the simple imidoyl isoimides (7) in solution to determine the effect of substituents on the aryl rings. However, because of the rapid nature of the [1,3] acyl migration, isolation of these imidoyl isoimides is not possible without the presence of two nitro-groups in the *N*-phenyl ring.



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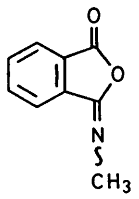

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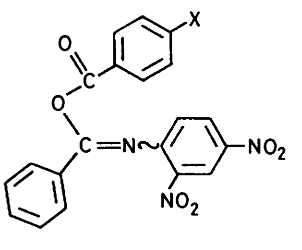

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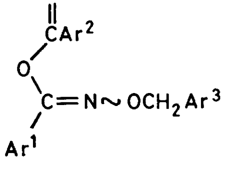
We now report a detailed study of these simple isoimides which were generated *in situ* by addition of the corresponding imidoyl chloride to a solution of the appropriate aliphatic or aromatic carboxylic acid in aqueous dioxan. The reaction proceeds *via* a nitrilium ion intermediate (Scheme). Detailed substituent effects have been obtained and on the basis of these and other results a reaction mechanism is presented.

RESULTS

O-Acylisoimides (10) are formed on addition of the corresponding imidoyl chlorides (8) to dioxan–water containing 0.1M sodium acetate, at 25 °C. The nitrilium ion (9) (Scheme) is trapped almost exclusively[10] by the acetate ion to give the isoimides (10) which then rearrange to the imides (11), *via* an O ⟶ N acyl migration. Product analysis (by u.v.) shows no trace of the amide (12). The [1,3] acyl migration of a number of isoimides, generated *in situ*, was conveniently followed spectrophotometrically.

(a) *Kinetics of the Rearrangement of* (10).—The isoimide (10) rearranges quantitatively to (11), in 1 : 1 dioxan–water (v/v), at pH 7. Subsequent analysis of the pH profile showed that the reaction was independent of pH over a wide region (Figure 1). At pH values below 4.5, rapid acid-catalysed hydrolysis of the isoimide (10), to the amide (12) occurs. The imide (11), however, is stable at low pH. Above pH 11.5 base-catalysed hydrolysis of the imide (11) occurs, which makes measurement of the rearrangement



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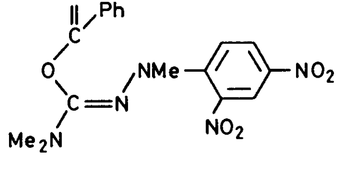

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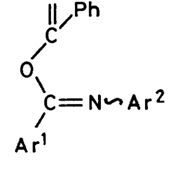

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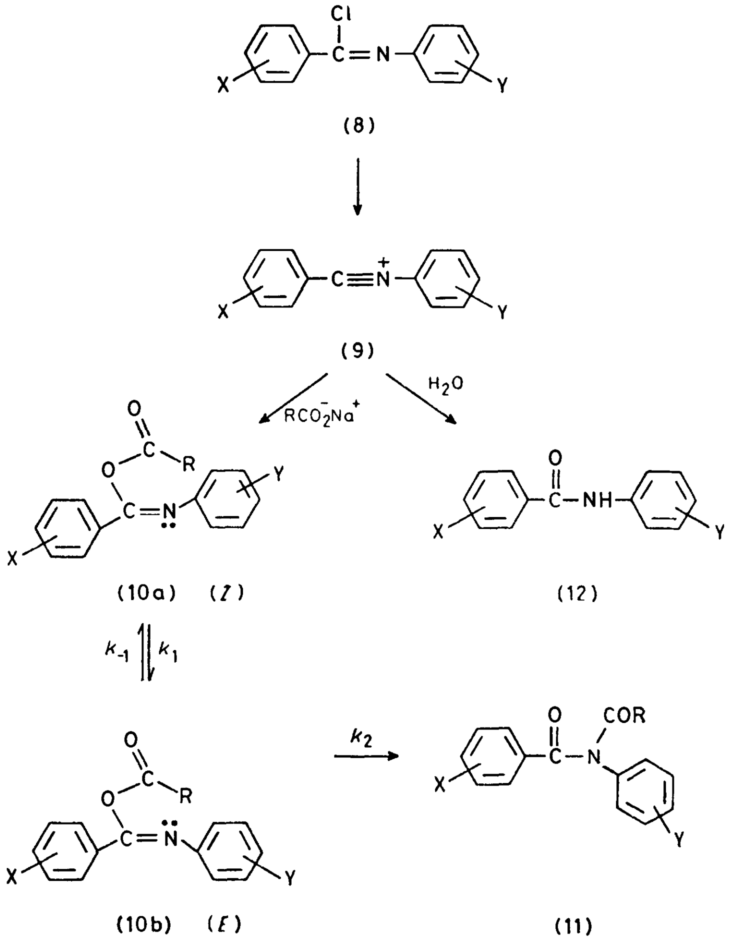


Scheme

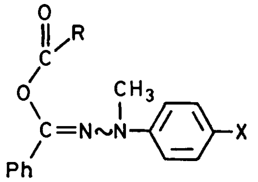
difficult in this pH region. This was confirmed by measuring the rate of hydrolysis of an authentic sample of the imide (11) (the data are included in Figure 1). The 'working' pH region where the rearrangement (10) ⟶ (11) alone occurs is effectively 6—11, and all subsequent studies reported were carried out in this region.

Table 1

The effect of the solvent on the rate of rearrangement of (10) ⟶ (11), at 25 °C in water–dioxan

% Dioxan (v/v)	$10^3k_{obs.}/s^{-1}$	Y[11]
90	4.89	−2.030
80	6.64	−0.833
50	15.07	1.361
20	32.39	2.877
0	44.30	3.493

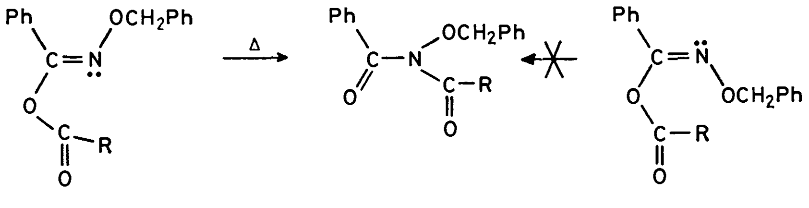
(b) *Solvent Effects.*—The rearrangement is also relatively insensitive to changes in solvent composition (Table 1) as can be seen from the Grunwald–Winstein m[11] value of 0.175. This low value is consistent with the intramolecular nature of the reaction.[12] Also the same rate constant was obtained in the presence of various sodium acetate concentrations, confirming the absence of competing intermolecular acyl-transfer reactions.



(13) X = H

(14) X = NO_2

The efficacy of this method of studying the O ⟶ N acyl migration can be gauged by comparing the rate constants of rearrangement of isoimides which were actually isolated with those for compounds formed by the above method. McCormack and Hegarty[8] have found that the



(15) (E) (16) (17) (Z)

TABLE 2

First-order rate constants for the rearrangement of isoimides (10; X = H) to imides (11; X = H) in 1 : 1 dioxan–water, at pH 7

R	Y	$10^2k_{obs.}/s^{-1}$	t/°C
$ClCH_2$	H	37.7	25
$\overset{+}{N}H_3CH_2$	H	14.4	25
CH_3OCH_2	H	11.1	25
CH_3CH_2	H	2.2	25
$ClCH_2CH_2$	H	1.7	25
CH_3	H	1.4	25
$3\text{-}NO_2C_6H_4$	H	5.77	25
$3\text{-}ClC_6H_4$	H	3.89	25
$4\text{-}ClC_6H_4$	H	2.87	25
Ph	H	2.22	25
$3\text{-}CH_3C_6H_4$	H	1.53	25
$4\text{-}CH_3C_6H_4$	H	1.15	25
$4\text{-}CH_3OC_6H_4$	H	0.77	25
$3\text{-}NO_2C_6H_4$	$p\text{-}NO_2$	14.78	55
$3\text{-}ClC_6H_4$	$p\text{-}NO_2$	8.73	55
$4\text{-}ClC_6H_4$	$p\text{-}NO_2$	7.94	55
Ph	$p\text{-}NO_2$	5.27	55
$3\text{-}CH_3C_6H_4$	$p\text{-}NO_2$	4.65	55
$4\text{-}CH_3C_6H_4$	$p\text{-}NO_2$	3.84	55
$4\text{-}CH_3OC_6H_4$	$p\text{-}NO_2$	2.16	55

rearrangement rate constant of (14; R = Me) in chlorobenzene at 55 °C is 1.8×10^{-4} s^{-1} (measured by n.m.r.). This compares with a value of 1.96×10^{-4} s^{-1}, for (14) formed *in situ* at pH 7, in 1:1 dioxan–water (55 °C).

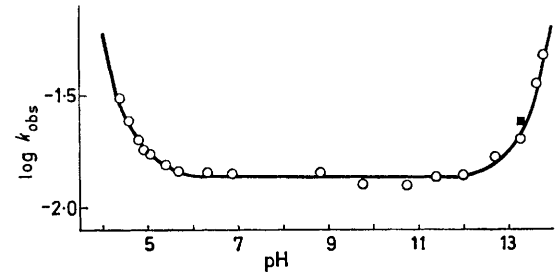


FIGURE 1 Plot of log of the observed rate constants ($k_{obs.}/s^{-1}$) for the reaction of the isoimide (10; X = Y = H) in 1 : 1 dioxan–water at 25°. The pH-independent reaction is conversion to the imide (11); acid and base catalysed hydrolysis are also observed at high and low pH. The rate of hydrolysis of the imide (11; X = Y = H, R = Me) is also included in this plot (datum point, ■)

(c) *Substituent Effects*.—The effect of varying the substituents in the migrating group on the rearrangement, is given in Tables 2 and 3; R was either an aryl or alkyl group. For the substituted acetyl derivatives, inductive electron withdrawal from the carbonyl group increases the rate of reaction. However, the correlation between rate constants and σ* values is poor (Figure 2) and factors other than inductive effects are clearly operative in the rearrangement.

TABLE 3

First-order rate constants for the rearrangement of the *Z*-isoimides (13) and (14) to the corresponding imides at pH 7, in 1 : 1 dioxan–water, at 55 °C

Compound	R	$10^4k_{obs.}/s^{-1}$
(13)	CH_3	10.24
(13)	Ph	9.83
(14)	CH_3	1.96
(14)	Ph	1.98

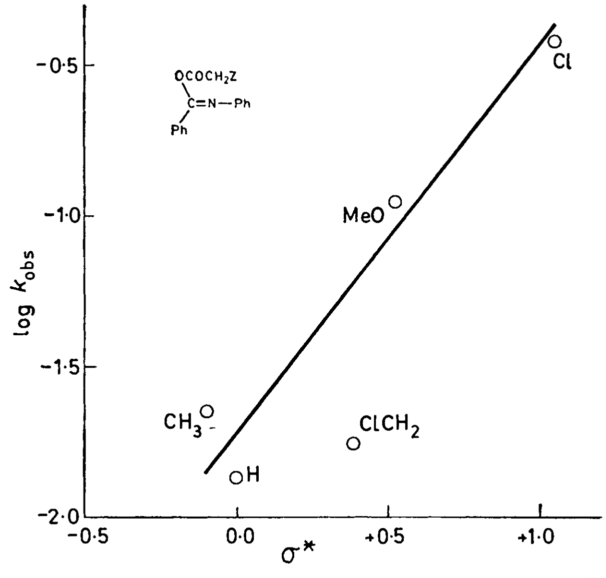


FIGURE 2 Plot of log $k_{obs.}$ for rearrangement of isoimides (10; X = Y = H, R = ZCH_2) as a function of the inductive σ* value of the substituent Z (1 : 1 dioxan–water; 25°)

On changing from an acetyl (10; X = Y = H, R = CH_3) to a benzoyl (10; X = Y = H, R = Ph) group, the rate of rearrangement is reduced by a factor of six (see Table 2), the same value which McCarthy and Hegarty [7] found for the rearrangement of (15) to (16).

Substitution in the aromatic ring in the migrating group also effects the reaction (Table 2). Electron-withdrawing substituents speed up the reaction and a Hammett plot of log $k_{obs.}$ *versus* the σ values [13] of the *m*- and *p*-substituents shows a break at H (Figure 3) giving ρ values of +0.60 and +1.65. However a similar Hammett plot for (10; X = H, Y = 4-NO_2) at 55 °C (Table 2) shows a break point at *p*-Me (Figure 3). Substituents in the *N*-aryl (Y) and the *C*-aryl (X) rings of (10; R = Me) have the same effect on the reaction, with substituents having $\rho_X = \rho_Y = -0.84$ (Figure 4).

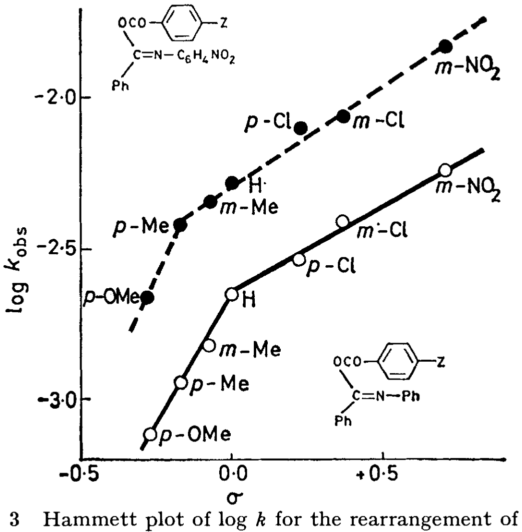
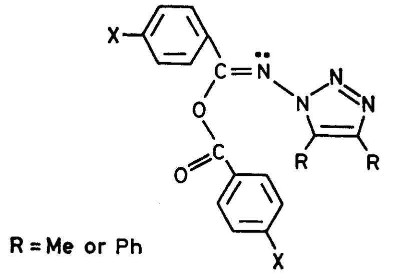


FIGURE 3 Hammett plot of log k for the rearrangement of (10) to (11) (R = ZC_6H_4, X = Y = H; solid line, ○ at 25°) and for (R = ZC_6H_4, X = H, Y = p-NO_2; broken line, ● at 55°) against ordinary σ values (solvent, 1 : 1 dioxan–H_2O); note temperature difference

DISCUSSION

Isoimides formed in solution by the nitrilium ion route (Scheme) have been shown to be formed stereospecifically [8] and exclusively in the Z-configuration (*i.e.* with the acyl group and the nitrogen lone pair *trans* to one another). X-ray crystallographic analysis,[8,14,15] and n.m.r. and dipole-moment studies [16] of the isoimides (6), (13), and (18) in solution have confirmed this.



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McCarthy and Hegarty,[7] by isolating both the Z- and E-isomers (15) and (17), showed that Z–E isomerization only occurred when the isomers were irradiated with u.v. light. Only the E-isomer (15), with its nitrogen lone pair correctly orientated, could undergo acyl transfer to (16) when heated. Because of the nature of the substituent attached to nitrogen (OR), (15) and (17) do not undergo thermal interconversion, so that the substituent effects observed for the conversion of (15) to (16) provide an unequivocal model for rate-determining intramolecular acyl transfer.[17]

On the other hand the isoimides (13) and (14) in the hydrazonyl series undergo slow thermal Z–E isomerisation and this has been shown to be the slow step for isoimide–imide rearrangements in this system.[8] This provides a model for the expected substituent effects on a rate-determining nitrogen inversion. For the isoimides (10), the rate of nitrogen inversion (and thus Z–E isomerisation) is greatly enhanced relative to that for (17) or (13) by the presence of an aromatic substituent attached directly to nitrogen.[18] Thus either step (Z–E isomerisation or acyl transfer) is potentially rate-determining in the present instance.

The Hammett ρ–σ correlations in Figure 3 clearly show that a change in rate-determining step takes place as the aryl substituent in the migrating aroyl group R in (10) is varied. Distinct breaks in the linear free energy relationships are observed both when Y = p-NO_2 and H. An alternative possibility that the curvature observed in Figure 3 is due to the use of inappropriate σ values can be discounted. The substituents were carefully chosen to include electron-withdrawing and -donating *meta*-substituents (whose σ^+ or σ^- values are almost the same as ordinary σ values). A distinctly poorer correlation is obtained when the log $k_{obs.}$ values are plotted against σ^+; moreover it is difficult to visualise how electron donation by resonance from the R group could stabilize the transition state for either Z–E isomerisation (k_1, Scheme) or rate-determining acyl transfer to nitrogen (k_2).

The six-fold rate enhancement on changing from (10; R = Ph) to (10; R = Me) (X = Y = H) indicates that in both these substrates, nucleophilic attack (rather than Z–E isomerisation) is rate-determining. This enhancement is less that the typical values (attributed to a combination of steric effects and resonance-stabilization of the benzoyl group) for intermolecular reactions [19] but is the same as that reported for the conversion of (15) into (16), an unequivocal intramolecular acyl transfer.[7] We have also tested this criterion by using an acyl transfer whose rate is known to be limited by substrate Z–E isomerisation; with both (13) and (14) (Z isomers) the *same* rate of O $\longrightarrow$ N acyl transfer was observed independently of whether R was Me or Ph (see Table 3). The $k_{obs.}$(Me) : $k_{obs.}$(Ph) ratio (*ca.* 6 for rate-determining acyl transfer, *ca.* 1 when Z–E isomerisation is rate-determining) therefore appears to be a useful probe for the determination of the slow step in these isomerisations.

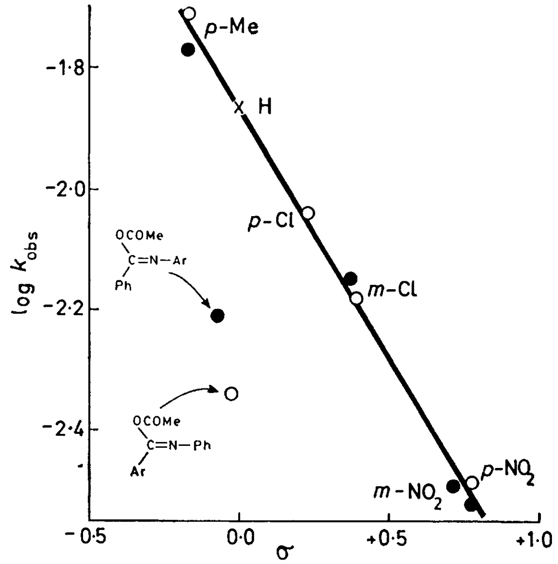


FIGURE 4 Hammett plot for rearrangement of (10) to (11) (R = Me, Y = H, X varies; ○) and (R = Me, X = H, Y varies; ●) at 25° in 1 : 1 dioxan–water; × is a point common to both series. The line is drawn with slope −0.84

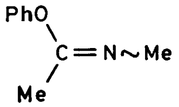
The substituent effects of X and Y for the conversion of (10; R = Me) to (11; R = Me) are also inconsistent with rate-determining Z–E isomerisation. For the latter, several studies have shown that the expected ρ_X would be 0 ± 0.5 [8,20–22] and ρ_Y *ca.* $+2$,[20,23,24] quite different from the observed values (Figure 4) of $\rho_X = \rho_Y \sim -0.8$. For rate-determining nucleophilic attack, taking the conversion of (15) into (16) as a model, the expected ρ values are -0.5 and -0.9 for substituents X and Y respectively [7] which are of the same sign and magnitude as those observed for (10) $\longrightarrow$ (11).

The same rate-determining step (10b) $\longrightarrow$ (11) appears to be operative when the migrating group R is an aroyl group carrying an electron-withdrawing substituent. This is reasonable on the basis that k_2 should be depressed whereas k_1 should remain unchanged when R is changed from Me to Ph. With electron-withdrawing substituents in R, the observed ρ value is $+0.60$. This is consistent with nucleophilic attack (k_2) as the rate-determining step [the ρ value for the migrating group in the conversion of (15) into (16) is $+0.65$].[7] However, this ρ value does not rule out rate-determining *Z–E* isomerism (k_1), since the expected ρ value is of much the same magnitude (actually $+0.77$).[8] However, any mechanism involving a pre-equilibrium [with (10b) in steady-state concentration or in a small equilibrium concentration with (10a)] can be ruled out, although this may occur (see below) when R is changed to an electron-donating group.

The breakdown which occurs in the Hammett plots (see Figure 3) could most obviously be due to a change from k_2 to k_1 as rate limiting (Scheme). We believe that this is unlikely, however, since (*a*) both k_1 and k_2 are affected to much the same degree by a change in the group R (as judged from the ρ values for model systems) and (*b*) the ρ value observed for electron-withdrawing substituents in R ($+1.65$) is over twice that expected for slow *Z–E* isomerisation.

We therefore conclude that when R is electron withdrawing, the equilibrium between (10a) and (10b) is rapidly established on dissolution; this equilibrium lies largely to the side of the *E*-isomer, so that substituent effects act only on k_2. However when R is electron donating, the equilibrium between (10a) and (10b) lies towards the starting (*Z*)-isoimide (10a) and varies with substituents. The observed ρ value will then depend on the sum of the ρ values for the equilibrium (k_1/k_{-1}) and for nucleophilic attack (k_2). Although the substituent effect on the equilibrium (k_1/k_{-1}) cannot be measured directly, we can estimate this as $\rho \geqslant +0.77$ [the value for k_1 for (13)]; on this basis the predicted ρ value for a mechanism involving rate-determining k_2 preceded by an *Z–E* equilibrium which lies to the side of the unreactive *Z*-isomer, is $\geqslant +1.42$, which compares favourably with the observed value of $+1.65$.

This interpretation implies that electron donation in R shifts the equilibrium (k_1/k_{-1}) between (10a) and (10b) towards the *Z*-form (10a), which is consistent with the known effect on the rate constant (k_1) of *Z–E* isomerisation of isoimides.[8] It also implies that *Z–E* equilibration is fast in all cases relative to O $\longrightarrow$ N acyl transfer. This is probably true since *N*-arylimines equilibrate rapidly at ambient temperatures,[20] while *N*-alkylimidates (19)[25] and iminocarbonates[26,27] (20) also undergo *Z–E* equilibration rapidly at 25°.



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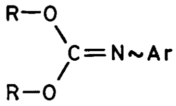

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Finally, the position of the ' break ' in the Hammett plot shows a distinct change between the two series (10; Y = H) and (10; Y = *p*-NO$_2$) (see Figure 3). The *N*-*p*-nitrophenyl group is known to enhance imine equilibration rates[20] (k_1, Scheme); thus only the most strongly electron-donating substituents in R (R = *p*-MeOC$_6$H$_4$) are able to slow equilibration between (10a) and (10b).

When the migrating group R is aliphatic, the same general trend (increasing rate of rearrangement as the electron-withdrawing power of R is increased) is observed (see Figure 2). However there is a good deal of scatter in the plot of log $k_{\text{obs.}}$ against the σ^* values (the line has been drawn with a slope, or ρ^* value, of $+1.27$). This is most likely a result of the operation of steric effects in the highly restricted transition state required by the acyl group migration.

In conclusion, the trapping procedure described in this report permits the study in solution of a wide variety of hitherto unobtainable isoimides. The materials (4) isolated by Curtin and Miller[6] are those for which the slowest rates of rearrangement can be expected. Our substituent effects in the migrating group R (when k_2 is rate-determining) are similar to that ($+0.69$) measured in benzene[6] for substituents X similarly placed in (4). However, our more extensive data show a clear break in the linear-free-energy plot; we conclude that this occurs since, although O $\longrightarrow$ N acyl transfer is rate determining in all cases, the pre-equilibrium between the *Z*- and *E*-forms of the isoimide becomes kinetically important when *R* contains electron-donating groups.

EXPERIMENTAL

All inorganic materials were AnalaR grade and used as received. M.p.s were determined on a Thomas–Hoover capillary m.p. apparatus and are uncorrected. I.r. spectra were recorded on a Perkin-Elmer 257 spectrophotometer and the ^{1}H n.m.r. spectra were obtained on a Perkin-Elmer R20-A spectrometer operating at 60 MHz with tetramethylsilane as internal standard.

Substrates.—The general experimental procedures for the synthesis of the substituted imidoyl chlorides,[28] the *N*-aryl-*N*-methylbenzohydrazonyl chlorides,[8] and the *N*-aryl-*N*-methylbenzohydrazides[8] are as previously described.

The sodium salts of the substituted benzoic acids were generated *in situ* by adjusting the pH of the solution to 7 with NaOH (1M).

N-Acetylbenzanilide (11) was prepared by addition of *N*-phenylbenzimidoyl chloride to a slurry of silver acetate in dry methylene chloride. The mixture was stirred overnight at ambient temperature and the silver salts were then filtered off. The oil, obtained on removal of the solvent, solidified on standing. This was recrystallized from petroleum (b.p. 40—60°) and had m.p. 62—63° (lit.,[29] 82°) (Found: C, 75.7; H, 5.4; N, 5.8. Calc. for $C_{15}H_{13}NO_2$: C, 75.3; H, 5.4; N, 5.9%).

N-*Methyl*-N-*phenyl*-4-*nitrobenzohydrazonyl chloride*. Finely ground phosphorus pentachloride (2.10 g) was added slowly to a suspension of *N*-methyl-*N*-phenyl-4-nitrobenzohydrazide (2.50 g) in dry benzene (100 ml). On addition of all the phosphorus pentachloride the solution went clear and the colour changed from yellow to dark red. Stirring was continued for 2.5 h, and the solution was then refluxed for 30 min. Removal of the solvent and phosphoryl chloride under reduced pressure gave a dark brown oil. On addition of petroleum (b.p. 40—60°) and cooling the solution in an ice-bath, a *solid* resulted (1.76 g, 65%), m.p. 67—69° (Found: C, 58.8; H, 4.35; Cl, 12.3; N, 14.2. $C_{14}H_{12}ClN_3O_2$ requires C, 58.05; H, 4.15; Cl, 12.25; N, 14.51%).

Kinetic Method.—The water was doubly distilled using a Fi-Streem bi-distillation unit. Reagent-grade dioxan was purified by the method of Vogel [30] and solvent mixtures were prepared by mixing appropriate volumes of the components.

The course of the rearrangement was followed on a Unicam SP 800, a Perkin-Elmer 124, or a Beckman model 25 u.v. spectrophotometer. Repetitive scans of the u.v. region established suitable wavelengths at which an appreciable optical density change occurred during the reaction. The solvent mixture, containing a 0.1M solution of the appropriate sodium salt, was equilibrated for 10 min before each kinetic run. Reactions were initiated by injecting 5—10 μl of substrate (1×10^{-1}M), in purified dioxan, into this cell. The rates of rearrangement were generally measured at pH *ca.* 7 in the absence of added buffer and first-order rate constants were calculated by using the experimental infinity values. To verify the pH-independence of these rates, the reaction was also carried out at pH 6 and 8 and the values reported in the Tables are averages of at least three determinations and show a standard deviation of <4%. A Radiometer PHM 26 pH meter and Metrohm EA 125 U glass electrode were used to measure the pH of the dioxan–water solutions. In all cases the electrode was allowed to equilibrate in each dioxan–water solution for 5 min before a reading was taken.

Product Analysis.—The product of the rearrangement of (10) was confirmed as the corresponding imide (11) both by comparing the u.v. spectrum obtained at the completion of the kinetic experiment with the spectrum of an authentic sample of the imide measured under the same conditions, and by actual isolation when the reaction was carried out on a synthetic scale.

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