*The Cyclodehydration of Anils. Part I. Kinetics of Cyclodehydration of 2-Anilino- and 2-*p*-Toluidino-pent-2-en-4-one in Sulphuric Acid.*

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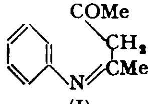
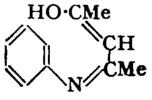
The rates of cyclodehydration of 2-anilino- and 2-*p*-toluidino-pent-2-en-4-one have been measured in aqueous sulphuric acid in the range 84·5—97·3% H_2SO_4. The first-order rate constants (k_1) for a fixed initial 0·1M-concentration of condensation product are related to the acidity function, H_0, by Hammett's equation $\log k_1 + H_0 =$ constant. An approximately linear relation is found between k_1 and the molar ratio $[H_2SO_4]/[HSO_4^-]$. This relation also applies to the rate constants determined in ammonium sulphate–sulphuric acid if it is assumed that the NH_4^+ ion has a solvation number of 1 in sulphuric acid.

The formation of 2 : 4-dimethylquinolines when the condensation products of acetylacetone and primary arylamines are heated in sulphuric acid was first investigated by Combes (*Compt. rend.*, 1887, **106**, 142; *Bull. Soc. chim.*, 1888, **49**, 90). The influence of substituent groups in the aromatic nucleus on this cyclodehydration reaction was examined by Turner and Roberts (*J.*, 1927, 1836), and their results, together with subsequent work on cyclodehydration, have been summarised by Bradsher (*Chem. Rev.*, 1946, **38**, 447).

The condensation products are usually represented as tautomeric ketimine (I or II) and enamine (III) structures; *e.g.*, the last is 2-anilinopent-2-en-4-one. From a study of the molecular refractivity of this anil, using both the pure compound and its solution in methylnaphthalene, von Auwers and Susemihl (*Ber.*, 1930, **63**, 1072) obtained exaltations of 3·5 for the pure compound and 3·35 for the solution above the value calculated for structure (III). They concluded that the anil has this structure, since there exists conjugation between the C=C bond and C=O group and between the nitrogen atom and the benzene ring. However, comparison of the calculated molecular refractivities of the forms (II) and (III) shows that they differ only in the contribution of the nitrogen and the oxygen atoms which are differently bound in the two structures. The molecular refractivity values for these contributions are shown below [values taken from von Auwers and Susemihl (*loc. cit.*) and Gilman's " Organic Chemistry," John Wiley & Sons, Ltd., 2nd Edn., 1943, Vol. II, p. 1751]. The difference of only 0·135 therefore does not permit a decision between the two structures.



(I)



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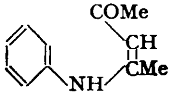

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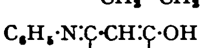
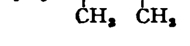
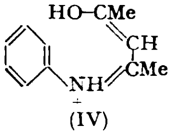
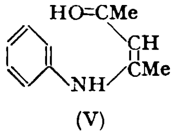
 $C_6H_5\cdot NH\cdot \underset{CH_3}{C}{:}CH\cdot \underset{CH_3}{C}{=}O$	Secondary N atom	2·499	4·710
	=O	2·211	
 $C_6H_5\cdot N{:}\underset{CH_3}{C}\cdot CH{:}\underset{CH_3}{C}\cdot OH$	–N=	3·05	4·575
	–O–	1·525	

The ketimine structure has been proposed in cases where failure to cyclise under the usual conditions has been observed; *e.g.*, since the products from aniline and formylacetone (Thielpape, *Ber.*, 1922, **55**, 127) and from *p*- and *o*-chloroaniline and acetylacetone (Turner and Roberts, *loc. cit.*) could not be cyclised in acidic media, it was suggested that they exist in the *trans*-form of the ketimine, which is sterically unsuited to cyclisation. Edwards and Petrow (*J.*, 1954, **2853**) recently dealt with this point and from infrared-spectral studies concluded that the products from *o*-, *m*-, and *p*-chloroaniline and acetylacetone are in the ketimine form; of these only the *m*-compound cyclises in sulphuric acid (Turner and Roberts, *loc. cit.*).

It is reasonable to assume that in the acid media employed for cyclodehydration the reacting form is cationic, and the same cationic resonance structures (IV)—(VI) can be derived from structure (II) or (III) by proton uptake.


(IV)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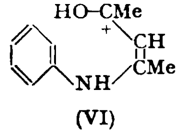
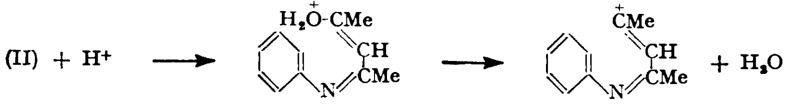

(VI)

Similar cationic structures in other cyclisations in acid media have been suggested by Petrow (*J.*, 1942, 693), Berliner (*J. Amer. Chem. Soc.*, 1944, **66**, 533), and Morley and Simpson (*J.*, 1948, 2024).

An alternative but more remote possibility is that the anil in the form (II) ionises in sulphuric acid as follows:


(VII)

A decision between the alternative cationic species represented by (IV)—(VI) and (VII) can be made by examining the relations between the rate constant of the cyclodehydration and Hammett's acidity function H_0 and the J_0 function defined by Gold and Hawes (*J.*, 1951, 2102). Hammett and Deyrup (*J. Amer. Chem. Soc.*, 1932, **54**, 2721) showed that if a reaction in sulphuric acid is of the first order and the reacting species is formed by uptake of a single proton from the medium without further modification of the cation which results, then, provided there is only a relatively small fraction of the compound present in its cationic form, the experimental rate constant k_1 and the acidity function H_0 are related by the equation $\log k_1 + H_0 =$ constant, where $H = -\log \alpha_{H^+}f_B/f_{BH^+} = pK + \log [B]/[BH^+]$, K representing the acid dissociation constant, and [B] and [BH$^+$] the concentration of un-ionised and ionised form of a base indicator ionising in the medium by simple proton uptake. This is in effect equivalent to demonstrating the constancy of the sum of $\log k_1$ and the logarithm of the ionisation ratio [B]/[BH$^+$] of a simple basic indicator ionising over the range of media for which kinetic data are obtainable.

If on the other hand the cyclisation occurs in the cationic species represented by structure (VII), then a similar type of relation can be deduced between k and the ionisation ratio [ROH]/[R$^+$] of a triphenylmethanol-type indicator which ionises according to the sequence

$$\mathrm{ROH} \overset{\mathrm{H^+}}{\rightleftharpoons} \mathrm{ROH_2^+} \rightleftharpoons \mathrm{R^+} + \mathrm{H_2O} \quad . \; . \; . \; . \; . \; . \; . \quad (1)$$

Let $[A]_T$ represent the concentration of the total amount of " anil " present, [A$^+$] that present as the cation (VII), and [A] that of the residual " anil." The theoretical rate equation (for a first-order reaction) is given by $k_0[A^+]f_{A^+}/f_{tr}$, where f_{tr} is the activity coefficient of the transition complex. Assuming that the activity coefficient ratio f_{A^+}/f_{tr} is constant over the range of media investigated, and equating with the experimental rate equation, we have:

$$k_1[A]_T = k[A^+] \text{ where } k = k_0f_{A^+}/f_{tr} \quad . \; . \; . \; . \; . \; . \quad (2)$$

or

$$\log k_1 + \log [A]_T/[A^+] = \log k \quad . \; . \; . \; . \; . \; . \quad (3)$$

For alcohols ionising in the form of equation (1) it has been shown (Murray and Williams, *J.*, **1950**, **3318**) that the difference between the logarithms of the ionisation ratios of two such compounds over narrow ranges of sulphuric acid–water media is a constant. If the same relation holds for an " anil " ionising as in (1) we can write :

$$\log [\mathrm{A}]/[\mathrm{A}^+] - \log [\mathrm{ROH}]/[\mathrm{R}^+] = \text{constant (independent of medium)} \quad . \quad (4)$$

where ROH represents a triphenylmethanol indicator ionising in the range of media in which the rates of cyclisation have been measured. If the extent of conversion of the compound A into its cation A^+ is very small, *i.e.*, $[\mathrm{A}^+] \ll [\mathrm{A}]$ so that [A] is approximately the same as $[\mathrm{A}]_\mathrm{T}$, we have by combining (3) and (4) :

$$\log k_1 + \log [\mathrm{ROH}]/[\mathrm{R}^+] = \text{constant} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

A correlation of this kind between the rate of nitration of benzene and the ionisation ratio for 4 : 4′ : 4″-trinitrotriphenylmethanol in sulphuric acid, found by Westheimer and Kharasch (*J. Amer. Chem. Soc.*, 1946, **68**, 1871), provided evidence that the nitric acid ionised according to (1) to produce the nitronium $\mathrm{NO_2}^{+\cdot}$ ion. A more general form of equation (5) is :

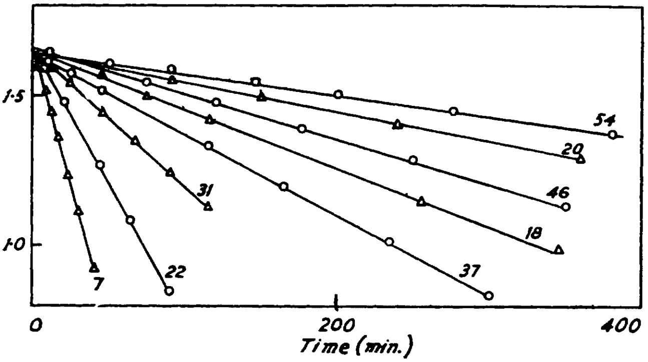


FIG. 1.
○ 2-*Anilinopent-2-en-4-one.*
△ 2-p-*Toluidinopent-2-en-4-one.*

$$\log k_1 + J_0 = \text{constant} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where J_0, as defined by Gold and Hawes (*loc. cit.*), is given by $J = -\mathrm{p}K_{\mathrm{ROH}} + \log [\mathrm{ROH}]/[\mathrm{R}^+]$. Equation (6) has been shown to apply to the nitration of the p-$\mathrm{C_6H_4Me{\cdot}NMe_3}^+$ ion in sulphuric acid (Lowen, Murray, and Williams, *J.*, 1950, **3318**) and to the decarbonylation of triphenylacetic acid in sulphuric acid (Deno and Taft, *J. Amer. Chem. Soc.*, 1954, **76**, 244, from results obtained by Dittmar, *J. Phys. Chem.*, 1929, **33**, 533). In the present paper, equation (5) is preferred to equation (6) as a test of this mechanism, since an agreed scale of J_0 values over a sufficient range of media is not yet available (see Williams and Bevan, *Chem. and Ind.*, 1955, 171, and Gold, *ibid.*, p. 172).

Kinetics of the Cyclodehydration.—The rates of conversion of 2-anilino- and of 2-*p*-toluidino-pent-2-en-4-one into 2 : 4-dimethyl- and 2 : 4 : 6-trimethyl-quinoline in aqueous sulphuric acid were followed by hydrolysis of the unchanged compound at known intervals of time to the aromatic amine and acetylacetone, and colorimetric estimation of the latter by conversion into ferric acetylacetone in aqueous acid. Excellent first-order rate constants were obtained for both compounds in the range of media studied as shown in Fig. 1. The rate constant depends to a slight extent on the initial concentration of the " anil "; this is a feature of other reactions in sulphuric acid, *e.g.*, nitration, and will form the subject of a separate study. All results quoted in this paper have been obtained with an initial 0·1M-concentration of organic reactant. The results for the anilino- and the *p*-toluidino-compounds are shown in Table 1. The H_0 values were taken from a curve obtained by plotting the experimental H_0 values (quoted by Deno and Taft, *loc. cit.*) against percentage of sulphuric acid, and the log [ROH]/[R⁺] values were similarly obtained from the results of the investigation of the ionisation of 4 : 4′ : 4″-trinitrotriphenylmethanol (Murray and Williams, *loc. cit.*). It is clear that the ($\log k + H_0$) values are reasonably constant for both compounds, while there is a marked variation in the ($\log k + \log [\text{ROH}]/[\text{R}^+]$) values. It can be concluded that the products cyclise in the form of simple cationic structures resulting from uptake of a single proton without further change in the ionic species.

First-order rate constants were obtained in the decarbonylation of aromatic aldehydes (Schubert and Zahler, *J. Amer. Chem. Soc.*, **1954**, **76**, 1) and in the decarboxylation of aromatic acids (Schubert, Donohue, and Gardner, *ibid.*, p. 9) in sulphuric acid, but the authors concluded that the Hammett unimolecular mechanism does not apply to these reactions. In both reactions studied, extensive conversion of the aromatic compound (B) into its conjugate acid (BH^+) occurs in relatively aqueous acids (60—80% sulphuric acid) and a modified form of the Hammett equation was used, *viz.*,

$$\log k + H_0 - \log [\text{B}]/[\text{B}]_{\text{stoich.}} = \text{constant}$$

where [B] represents the concentration of un-ionised form and $[\text{B}]_{\text{stoich.}}$ the total concentration (all forms) of the aromatic compound. Since their results did not fit this equation, alternative bimolecular and termolecular mechanisms were considered and for the decarboxylation evidence was obtained for a bimolecular reaction between the aromatic compound and molecular sulphuric acid. A similar bimolecular mechanism was put forward by Sommer, Barie, and Gould (*ibid.*, **1953**, **75**, 3765) for the formation of methane from β-trimethylsilylpropionic acid in sulphuric acid; the ratio of the first-order rate constant for the evolution of methane to the concentration of molecular sulphuric acid was shown to be constant over the range 89—97% sulphuric acid, and Deno and Taft (*loc. cit.*) later established that the constancy of this ratio was maintained down to 85% sulphuric acid. There is no evidence of any such correlation in the cyclodehydration, and this particular bimolecular mechanism can be rejected for this reaction.

TABLE 1. *Rates of cyclodehydration in sulphuric acid–water media.*

2-Anilinopent-2-en-4-one					2-*p*-Toluidinopent-2-en-4-one				
Medium, % H_2SO_4	Expt. no.	10^2k_1 (min.$^{-1}$)	$\log k_1 + H_0$	$\log k + \log [\text{ROH}]/[\text{R}^+]$	Medium, % H_2SO_4	Expt. no.	10^2k_1 (min.$^{-1}$)	$\log k_1 + H_0$	$\log k + \log [\text{ROH}]/[\text{R}^+]$
97·3	22	2·11, 2·09	−10·79	—	95·5	95	8·49, 8·45	− 9·89	—
95·7	71	1·24, 1·22	−10·76	—	93·1	7	4·29, 4·28	− 9·91	−2·57
95·5	97	1·20, 1·21	−10·74	—	91·1	11	2·12, 2·12	− 9·98	−2·32
95·2	26	1·14	−10·72	—	89·2	13	1·22, 1·23	−10·00	−2·05
93·3	37	0·614, 0·622	−10·77	−3·46	89·0	31	1·06, 1·05	−10·01	−2·02
91·2	46	0·343, 0·341	−10·79	−3·15	87·6	24	0·742, 0·741	−10·05	−1·83
89·2	75	0·211, 0·210	−10·77	−2·80	86·3	18	0·445, 0·450	−10·10	−1·63
88·6	54	0·166, 0·163	−10·80	−2·75	85·5	27	0·330, 0·330	−10·13	−1·50
					84·5	20	0·238, 0·239	−10·14	−1·32

Relation between the Rate Constant and the Ratio $[H_2SO_4]/[HSO_4^-]$.—Brand (*J.*, 1950, 1002) has shown that Hammett's acidity function H_0 in the range 89—99·8% sulphuric acid can be calculated with the empirical equation

$$H_0 = -8·36 + \log [HSO_4^-]/[H_2SO_4] \quad . \quad . \quad . \quad . \quad . \quad (7)$$

if the reaction

$$H_2O + H_2SO_4 = H_3O^+ + HSO_4^- \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

is assumed to be complete. Deno and Taft (*loc. cit.*) later showed that equation (7) is applicable in the range of media 83—89% sulphuric acid if a value of 50 is assigned to the equilibrium constant, K, of reaction (8). As a consequence of the validity of this method of calculating H_0 values, these authors conclude that the activity coefficient ratio $f_{H_3O^+}f_{HSO_4^-}/f_{H_2O}f_{H_2SO_4}$ is constant over the range 83—100% sulphuric acid. From the constancy of the $\log k_1 + H_0$ addition in the cyclodehydration, it follows that for this reaction

$$\log k_1 - \log [H_2SO_4]/[HSO_4^-] = \text{constant} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

A simple derivation of equation (9) is possible from the following considerations. If the compound A is involved in the equilibrium

$$A + H_2SO_4 \rightleftharpoons AH^+ + HSO_4^- \quad . \ . \ . \ . \ . \ . \ . \quad (10)$$

with an equilibrium constant K' given by

$$K' = \frac{[AH^+][HSO_4^-]}{[A][H_2SO_4]} \frac{f_{AH^+}f_{HSO_4^-}}{f_A f_{H_2SO_4}} \quad . \ . \ . \ . \ . \ . \ . \quad (11)$$

then from equation (11) and the appropriate form of equation (3) in which $[A^+]$ is replaced by $[AH^+]$, assuming that $[AH^+] \ll [A]$ (*i.e.*, $[A]$ is approximately equal to $[A]_T$), we have

$$k_1 = kK'[H_2SO_4]/[HSO_4^-] \times \text{constant} \quad . \ . \ . \ . \ . \quad (12)$$

since the activity coefficient term is similar to that for the equilibrium (8) and can be expected to show the same constancy. The direct relation between the rate constant, k_1, and the ratio $[H_2SO_4]/[HSO_4^-]$ indicated in equation (12) is evident in Fig. 2, in which the curve represents the variation of $[H_2SO_4]/[HSO_4^-]$ with percentage of sulphuric acid; the values of the rate constants for both condensation products plotted (on suitable ordinate scales) against the percentage of sulphuric acid in the media in which they are determined lie very close to the curve. No parallelism is found with the curves of the variation of $[H_2SO_4]$ or $[HSO_4^-]$ with the percentage of sulphuric acid.

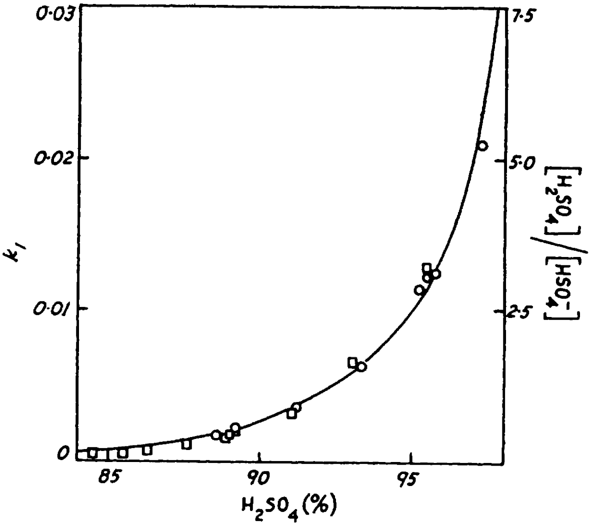


FIG. 2.
○ 2-*Anilinopent-2-en-4-one.*
□ 2-p-*Toluidinopent-2-en-4-one.*

A more stringent test of equation (12) is the demonstration that the plot of k_1 against $[H_2SO_4]/[HSO_4^-]$ is a straight line. This is shown in Fig. 3 and for both compounds reasonable linearity is evident. Also included in this Figure is the plot of k_1 against $[H_2SO_4]/[HSO_4^-]$ for the cyclodehydration of the *p*-toluidino-compound in water-free $(NH_4)_2SO_4$–H_2SO_4 media. The relevant results are shown in Table 2, where $[H_2SO_4]_T$ represents the stoicheiometric concentration of sulphuric acid, and $[H_2SO_4]$ the residual molecular sulphuric acid concentration. Each mole of ammonium sulphate requires 1 mole of sulphuric acid according to the equation $(NH_4)_2SO_4 + H_2SO_4 = 2NH_4^+ + 2HSO_4^-$ Although no simple correlation is found between k_1 and $[H_2SO_4]/[HSO_4^-]$ if this represents the sole interaction, yet the linear relation is obeyed if it is assumed that each ammonium ion binds 1 molecule of sulphuric acid by solvation. Evidence that this solvation occurs is provided by the freezing-point–composition data for $(NH_4)_2SO_4$–H_2SO_4 mixtures (Kendall and London, *J. Amer. Chem. Soc.*, 1920, **42**, 2135), which indicate the existence of a stable compound $(NH_4)_2SO_4,3H_2SO_4$, and the interpretation of the depression of freezing point of pure sulphuric acid by small amounts of ammonium sulphate by Gillespie, Hughes, and Ingold (*J.*, 1950, 2487) in terms of a solvation number of unity for the ammonium ion.

The constancy of the term in the last column of Table 2 is another expression of the relation given by equation (12) and shows in effect that the Hammett equation is obeyed although it cannot be tested directly since H_0 values have not been determined for $(NH_4)_2SO_4$–H_2SO_4 media.

TABLE 2. *Rates of cyclodehydration of* 2-p-*toluidinopent-2-en-one in* $(NH_4)_2SO_4$–H_2SO_4 *media.* (All concns. in moles/l.)

$(NH_4)_2SO_4$	k_1	$[HSO_4^-]$	$[H_2SO_4]_T$	$[H_2SO_4]$	$\frac{[H_2SO_4]}{[HSO_4^-]}$	$\log k_1 - \log [H_2SO_4]/HSO_4^-]$
1	0·131	2	17·42	14·42	7·21	−1·74
2	0·0554	4	16·14	10·14	2·54	−1·67
2·5	0·0314	5	15·47	7·97	1·59	−1·70
3	0·0172	6	14·80	5·80	0·97	−1·75
4	0·00298	8	13·36	1·36	0·17	−1·76

The gradient of each line in Fig. 3 represents the product of the constant terms in equation (12), and the ratio of the gradients for the two anils is the ratio of the *kK* products for each. The ratio *kK*(*p*-toluidino-compound)/*kK*(anilino-compound) obtained for the results in aqueous sulphuric acid is approximately 7, while the same ratio, from the results obtained for the *p*-toluidino-compound in ammonium sulphate–sulphuric acid, is *ca.* 5. The *p*-toluidino-compound cyclises more rapidly than the anilino-compound as a result of (i) the activating effect of the methyl group at the *meta*-position where ring closure occurs and (ii) the greater basicity of the nitrogen atom which is in the *para*-position to the methyl group. The rate of electrophilic substitution in aromatic compounds at the *meta*-position to a methyl group is about 2·5—3 times faster than in the unsubstituted benzene ring; this would account for about half the *kK* ratio found experimentally, the remainder presumably being the result of the greater basicity of the *p*-toluidino-compound.

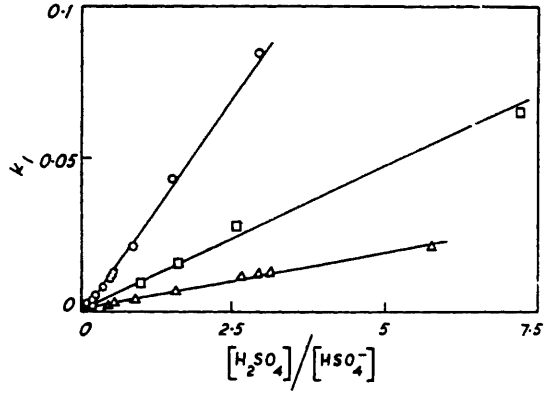


FIG. 3.

○ 2-p-*Toluidinopent-2-en-4-one in* H_2SO_4–H_2O.
△ 2-*Anilinopent-2-en-4-one in* H_2SO_4–H_2O.
□ 2-p-*Toluidinopent-2-en-4-one in* $(NH_4)_2SO_4$–H_2SO_4 (k_1 × 0·5).

EXPERIMENTAL

Materials.—Aniline and acetylacetone were distilled before use, and *p*-toluidine was crystallised twice from aqueous alcohol. The condensation products were prepared by Turner and Roberts's method (*loc. cit.*) and were recrystallised twice from light petroleum (b. p. 40—60°); 2-anilinopent-2-en-4-one had m. p. 50—52°; 2-*p*-toluidinopent-2-en-4-one had m. p. 65—66°.

Media.—Sulphuric acid–water mixtures were prepared by adding water or redistilled oleum to "AnalaR" concentrated sulphuric acid and standardised against N-sodium hydroxide referred through N-hydrochloric acid to potassium iodate. 100% Sulphuric acid was obtained by adjustment of a weak oleum to maximum freezing point. Water-free ammonium sulphate–sulphuric acid mixtures were prepared directly for each kinetic experiment by weighing the required amount of ammonium sulphate into a tared 50-ml. volumetric flask, adding 100%

sulphuric acid to dissolve the solid, and making up to the mark at 25°; the flask was then reweighed to obtain the weight of pure sulphuric acid present.

Conversion into Quinoline Compounds.—To establish that the cyclodehydration is practically quantitative under the conditions used for rate measurements, 1 g. of 2-anilinopent-2-en-4-one was rapidly dissolved in 10 ml. of 97·9% sulphuric acid (this corresponds to 5 times the concentration of organic reactant used in kinetic experiments) and kept at room temperature for 2 hr. The solution was poured into ice-cold water (100 ml.) and left for 2 hr. to ensure complete hydrolysis. The solution at 5° was treated with an ice-cold solution of sodium nitrite (0·05 g.) in water (5 ml.) to diazotise any aniline resulting from the hydrolysis, and then warmed to convert the diazonium salt into phenol. After cooling, sodium hydroxide (15 g.) was added to make the solution alkaline. The 2 : 4-dimethylquinoline was extracted with ether, and the ether extracts were washed with water and dried (Na_2SO_4). After filtration and evaporation, the crude product was obtained as a yellow liquid (yield 92%) (Found : C, 82·9; H, 7·2; N, 9·0. Calc. for $C_{11}H_{11}N$: C, 84·0; H, 7·05; N, 8·9%)

In a similar experiment, 2-*p*-toluidinopent-2-en-4-one (1 g.) was dissolved in a solution (10 ml.) of 1 mole/l. of ammonium sulphate in 100% sulphuric acid and kept for 2 hr. 2 : 4 : 6-Trimethylquinoline was recovered in 93% yield by the method described above (m. p. of crude product 40—41·5°; m. p. of pure compound 43—45°) (Found: C, 84·2; H, 8·0; N, 7·6. Calc. for $C_{12}H_{13}N$: C, 84·2; H, 7·65; N, 8·2%).

Analytical Method.—The condensation products could be determined by hydrolysis in *ca.* 2N-sulphuric acid to the aromatic amine and acetylacetone, followed by conversion of the latter into its soluble ferric complex; this is red and its solution obeys Beer's law (cf. Bonner and Thorne, *Analyst*, 1954, **79**, 759). The reagent is a 6·5% w/w solution of "AnalaR" ferric ammonium sulphate in 0·1N-sulphuric acid to which an aliquot portion of acetylacetone (1—2·5 mg.) in 0·1N-sulphuric acid is added. The colour is fully developed after 15 min., and the optical density of the solution is then determined on a "Hilger Spekker" photoelectric absorptiometer, a sodium filament lamp and a blue-green filter (No. 603) being used to confine the incident light to a wavelength band of 4700—5000 Å. The amount of acetylacetone present is read off from a standard curve obtained from measurements on solutions of known concentration. No interference occurs with aniline, *p*-toluidine, or the corresponding quinoline compounds, and the effect of sodium sulphate present in solutions from the kinetic experiments can be eliminated by obtaining the standard curve with acetylacetone solutions containing this salt. The results of analysis of pure 2-anilinopent-2-en-4-one are shown below. After hydrolysis with 2N-sulphuric acid each solution was made up to 500 ml., and the acidity adjusted to 0·1N. A suitable aliquot part was taken for the acetylacetone determination.

Reactant taken	Aliquot taken	Acetylacetone in aliquot :	
(g.)	(ml.)	Calc. (mg.)	Found (mg.)
0·2222	5	1·27	1·27
0·1295	10	1·48	1·50
0·0796	15	1·36	1·37

Procedure for Measuring the Rate of Cyclodehydration.—Kinetic measurements were carried out at 25° in a thermostat controlled to ±0·02°. The reaction vessel was a 100-ml. round-bottomed flask with a B24 neck. The organic reactant was weighed into a B24 socket cap, the amount taken providing a 0·1M-solution when dissolved in 50 ml. of the medium. The medium, previously made up to the mark in a tared 50-ml. volumetric flask at 25°, was transferred to the reaction vessel; 30 sec. were allowed for drainage, and the flask was reweighed to allow a correction to be made for incomplete transfer. To start the reaction, the reaction vessel was removed from the thermostat, and the filled socket cap inserted. The medium and reactant were brought into contact at zero time by vigorous shaking, and after complete dissolution had occurred (1—2 min.) the flask was returned to the thermostat. Air bubbles formed during the shaking were rapidly removed by replacing the socket cap with a B24 cone connected to a suction pump. As soon as the liquid was clear (1—2 min.) the cone and pump were detached and the flask was restoppered. Six to eight 2-ml. samples were taken from the reaction mixture in the course of a run. Each sample was drawn into 2-ml. pipette, having a wide delivery jet and previously standardised for delivery of sulphuric acid, and run into 20 ml. of ice-cold water. This dilution stopped the reaction and also provided an approximately 2N-sulphuric acid. After the mixture had been kept for 2 hr. at room temperature to ensure complete hydrolysis of unconverted anil, 2·5 g. of pellet sodium hydroxide were added to the ice-cold solution to neutralise the bulk of the acid present. The solution was finally adjusted to neutrality by successive titration with

N-sodium hydroxide, N-sulphuric acid, and 0·1N-sodium hydroxide (B.D.H. Universal Indicator paper); the proximity of the end-point is indicated by the separation of the quinoline. 5 Ml. of N-sulphuric acid were added, and the solution filtered into a 50-ml. volumetric flask and made up to the mark with washings. The solution, now 0·1N with respect to sulphuric acid, was analysed by adding a 5-, 10-, or 15-ml. aliquot portion to 5 ml. of the ferric ammonium sulphate reagent and dilution to a final volume of 20 ml. with 0·1N-sulphuric acid. The optical density was measured as described above against a blank prepared in the same way from 2 ml. of the pure medium. Reactions were followed up to about 80% change. Rate constants were obtained from the first-order rate equation $k_1t = 2{\cdot}303\ \{\log a - \log (a - x)\}$; k_1 (min.$^{-1}$), was obtained graphically from the plot of log V_a against t, where V_a is the volume of the standard acetylacetone solution equivalent to the amount of acetylacetone in each 2-ml. aliquot portion of the reaction mixture removed. Duplicate determinations were carried out and these rarely differed by more than 1%.

Test for Surface Catalysis Effects.—The rate of cyclodehydration of 2-anilinopent-2-en-4-one in 95·5% sulphuric acid at 25° was unaltered within the limits of experimental accuracy by the addition of a quantity of small glass balls (with and without this addition, rate constant = 0·0123 and 0·0121 min.$^{-1}$, respectively). The reaction thus occurs entirely in the homogeneous liquid phase.

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