

that the cuprous bromide catalyzed reaction of *tert*-butyl peresters with ethers leads to the formation of acyloxy intermediates which decompose under the experimental conditions to the corresponding organic acids and unsaturated ethers.

The implication of our results can therefore be summarized.

I. A common type of mechanism is involved in the peroxydisulfate oxidation of alcohols and ethers.

II. The reaction of the  $\alpha$ -oxyalkyl radicals with peroxydisulfate leads to the formation of pseudohemiacetal (from alcohols) or pseudoacetal (from ethers) intermediates. Therefore, the question concerning the transition state structure for  $k_3$  seems to be answered; the chain lengths and rate laws are sufficiently similar as to lead to the conclusion that attack on peroxydisulfate by the  $\alpha$ -oxyalkyl radical involves the carbon center.

III. The natures of the final products are related to the characteristics of the intermediates and to the experimental conditions. Yet, at the same time, the reaction kinetics are little influenced by the nature of the products.

### Experimental Section

All chemicals not described below were reagent grade. Experiments carried out at B. U. utilized distilled water. Those carried out at M. S. C. utilized distilled-deionized water. B. & A. reagent  $K_2S_2O_8$  was recrystallized twice from deionized water. Spectrophotometric grade dioxane (Aldrich) was used without further purification at B. U., whereas at M. S. C. Fisher reagent was purified as suggested by Fieser and Fieser.<sup>12</sup> Tetrahydrofuran (Mallinckrodt Analytical Reagent) was refluxed over KOH pellets and distilled before use. Ethyl ether (Allied, Reagent ACS) was distilled before use.

Kinetics were followed with a Cary 15 spectrophotometer (B. U.) or Beckman Acta V spectrophotometer (M. S. C.), or by the usual iodometric analysis. Rate constants were calculated as previously reported.<sup>2,3</sup> Rate constants calculated for duplicate runs with integrated plots usually agreed to  $\pm 5\%$  and rate constants obtained from initial slopes varied by  $\pm 8\%$ .

**Products.** The reaction mixture (an aqueous solution of  $K_2S_2O_8$  and a tenfold molar excess of ether in a rubber-stoppered flask) was maintained at 60° in a thermostatic bath. Aliquots of the reacting solutions were withdrawn with a syringe, to prevent contact with air, at suitable time intervals and analyzed by vpc (Aerograph 200, F.I.D., column 15% SE-30 on 80/100 mesh A/W, DMCS Trete Chromosorb, 15 ft  $\times$  0.25 in. o.d.) and mass spectral (Hitachi

Perkin-Elmer, RMU-6D single focusing, ionization 50 eV) techniques. The mass spectrometer and gas chromatograph were connected.

Compounds isolated were the 2,4-dinitrophenylhydrazone of acetaldehyde from ethyl ether oxidation and the osazone of glyoxal from the dioxane oxidation. Vinyl ethyl ether, *p*-dioxene, and 2,3-dihydrofuran (from ethyl ether, dioxane, and tetrahydrofuran, respectively) were identified by mass spectra. Both the mass spectra and gas chromatography showed abundant peaks not common to the reactant ethers. Details may be obtained on request.

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**Registry No.**—Peroxydisulfate, 15092-81-6; ethyl ether, 60-29-7; tetrahydrofuran, 109-99-9; dioxane, 123-91-1; copper, 7440-50-8.

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## Reaction Kinetics of 2- and 3-Furoyl Chlorides with Anilines in Benzene

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The reaction rates of 2- and 3-furoyl chlorides with substituted anilines have been measured in benzene at different temperatures. The reactions follow second-order kinetics. 2-Furoyl chloride reacts faster and 3-furoyl chloride slower than benzoyl chloride. The activation parameters and the slopes of the Hammett and Bronsted plots are similar to those of the reactions of benzoyl and 2- and 3-thenoyl chlorides with aniline. The reaction mechanism of 2- and 3-furoyl chlorides with aniline is the same as for the benzoylation reaction. A linear relationship is obtained plotting the  $\log k$  for the reactions of 2-thenoyl, 3-thenoyl, 3-furoyl, and benzoyl chlorides with aniline against the infrared carbonyl stretching bands in  $CCl_4$  of the acid chlorides.

Several studies have been carried out with the purpose of comparing the furan and thiophene rings reactivity with that of the benzene nucleus.

The acid-catalyzed rearrangement of substituted allyl alcohols shows that the furyl and thienyl groups behave as electron-donating substituents.<sup>1</sup> The carboxylic acids of

furan and thiophene are stronger than unsubstituted benzoic acid indicating that the inductive electron-withdrawing effect of the heteroatoms is prevailing here.<sup>2</sup> In the esterification of the two isomeric 2- and 3-furoic acids,<sup>3</sup> in the acid-catalyzed hydrolysis of furan and thiophene carboxylic acid esters,<sup>4</sup> and in the alkaline hydrolysis of 2- and 3-

**Table I**  
**Second-Order Rate Constants and Activation Parameters for the Reaction of 2-Furoyl Chloride with Meta- and Para-Substituted Anilines in Benzene**

No.	Registry no.	Substituent	pK <sub>a</sub> <sup>c</sup>	$k_2 \times 10^2$ , l. mol <sup>-1</sup> sec <sup>-1</sup>					E <sub>A</sub> <sup>a</sup>	Log A	ΔS* <sup>b</sup>		
				10°	15°	17.5°	25°	30°				35°	45°
1	62-53-3	H <sup>18</sup>	4.58		8.74		13.3		19.0	6.85	4.14	-41.6	
2	108-44-1	<i>m</i> -CH <sub>3</sub>	4.69	11.9		15.8	21.4		30.4	6.54	4.12	-41.6	
3	106-49-0	<i>p</i> -CH <sub>3</sub>	5.12	36.4		48.1	63.0	74.9		6.15	4.31	-40.8	
4	536-90-3	<i>m</i> -CH <sub>3</sub> O	4.20		6.32		9.18		14.0	7.00	4.11	-41.7	
5	108-42-9	<i>m</i> -Cl	3.34				0.740		1.24	1.79	8.33	3.98	-42.3
6	106-47-8	<i>p</i> -Cl	3.98		2.15		3.50		5.04	7.52	4.04	-42.0	
7	99-09-2	<i>m</i> -NO <sub>2</sub>	2.50				0.0783		0.132	0.221	9.77	4.05	-41.9

<sup>a</sup> In units of kcal/mol. <sup>b</sup> At 25°, in cal mol<sup>-1</sup> °K<sup>-1</sup>. <sup>c</sup> Reference 18.

**Table II**  
**Second-Order Rate Constants and Activation Parameters for the Reaction of 3-Furoyl Chloride with Meta- and Para-Substituted Anilines in Benzene**

No.	Substituent	pK <sub>a</sub> <sup>c</sup>	$k_2 \times 10^2$ , l. mol <sup>-1</sup> sec <sup>-1</sup>				E <sub>A</sub> <sup>a</sup>	Log A	ΔS* <sup>b</sup>
			15°	25°	35°	45°			
1	H <sup>18</sup>	4.58	2.53	4.09	6.35	8.11	4.56	-39.6	
2	<i>m</i> -CH <sub>3</sub>	4.69	3.95	6.92	9.50	7.76	4.50	-39.9	
3	<i>p</i> -CH <sub>3</sub>	5.12	10.6	16.3	23.7	7.10	4.41	-40.3	
4	<i>m</i> -CH <sub>3</sub> O	4.20	1.54	2.50	3.98	8.37	4.53	-39.8	
5	<i>m</i> -Cl	3.34		0.218	0.371	0.590	9.38	4.22	-41.2
6	<i>p</i> -Cl	3.98		0.883	1.450	2.210	8.64	4.29	-40.9
7	<i>m</i> -NO <sub>2</sub>	2.50		0.0219	0.0395	0.0698	10.92	4.34	-40.6

<sup>a</sup> In units of kcal/mol. <sup>b</sup> At 25°, in cal mol<sup>-1</sup> °K<sup>-1</sup>. <sup>c</sup> Reference 18.

thenoates and 3-furoates both the heteroaromatic nuclei are electron donating, whereas in the alkaline hydrolysis of 2-furoates the furyl group behaves as electron withdrawing.<sup>4-7</sup> The solvolysis of 1-arylethyl acetates<sup>8</sup> and of ethyl *p*-nitrobenzoates<sup>9</sup> and the isomerization of *cis*-2-styrylthiophene in aqueous sulfuric acid<sup>10</sup> all indicate that the furan and thiophene nuclei are electron donating, whereas the rearrangement of 2-2'-thenil is a clear manifestation of the electron-withdrawing nature of this nucleus.<sup>11</sup>

In summary, from the above discussion, it is evident that the furan and thiophene nuclei possess a dual electronic nature: electron donating or electron withdrawing.

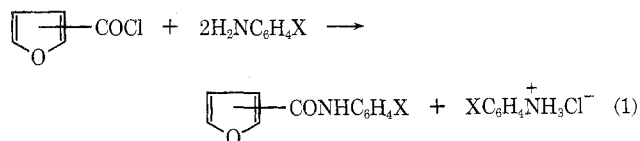
Recently we have undertaken an investigation of the reactions between 2-<sup>12</sup> and 3-thenoyl chlorides<sup>13,14</sup> and meta- and para-substituted anilines in benzene. We have found that 2- and 3-thenoyl chlorides reacted more slowly than benzoyl chloride, indicating the donating effect of the thienyl group.

In our preliminary note we reported the data relating to the reactions of 2- and 3-furoyl chlorides with aniline.<sup>13</sup> The reaction of 2-furoyl chloride was faster than that of benzoyl chloride, whereas 3-furoyl chloride reacted more slowly than the phenylic derivative. Thus, these results indicate that the furyl group behaves as electron withdrawing in the 2-furoyl chloride but as electron donating in the 3 analog compared to phenyl.

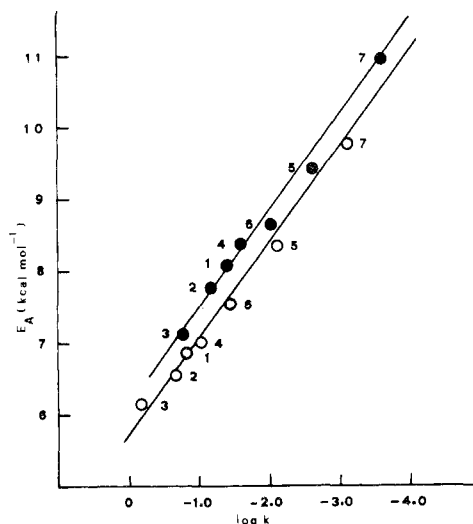
The purpose of the present paper is to amplify the study of the reactions of 2- and 3-furoyl chlorides with meta- and para-substituted anilines in benzene.

### Results and Discussion

The reactions of the 2- and 3-furoyl chlorides with meta- and para-substituted anilines take place quantitatively according to the stoichiometric eq 1. The reactions were fol-



X = H, *m*-CH<sub>3</sub>, *p*-CH<sub>3</sub>, *m*-CH<sub>3</sub>O, *m*-Cl, *p*-Cl, *m*-NO<sub>2</sub>



**Figure 1.** Plots of the experimental values of  $E_A$  against  $\log k_{25}$  for the reactions of 2- and 3-furoyl chlorides with anilines. The lines are of theoretical slopes  $-2.303RT$ .

lowed kinetically as previously described,<sup>13,14</sup> and in all cases the compounds gave excellent second-order kinetics.

The second-order rate constants, reported in Tables I and II, show that electron-donating substituents accelerate and electron-withdrawing groups retard the reactions: the 2-furoyl chloride reaction is faster than that of 3-furoyl chloride. The results compared with those of benzoyl chloride reaction<sup>15-17</sup> indicate that 2-furoyl chloride (Table I) reacts faster and 3-furoyl chloride slower (Table II) than benzoyl chloride.

The activation parameters, listed in Tables I and II, show a regular variation with the substituent in the aniline. In the 2- and 3-furoyl chloride reactions, as previously noted,<sup>14</sup> the effect of the substituents in the aniline is to modify the activation energy while  $\log A$  remains approximately constant. This is evident from Figure 1 where  $\log k$  at 25° for 2- and 3-furoyl chlorides is plotted against the experimental values of  $E_A$ . All the points lie close to the

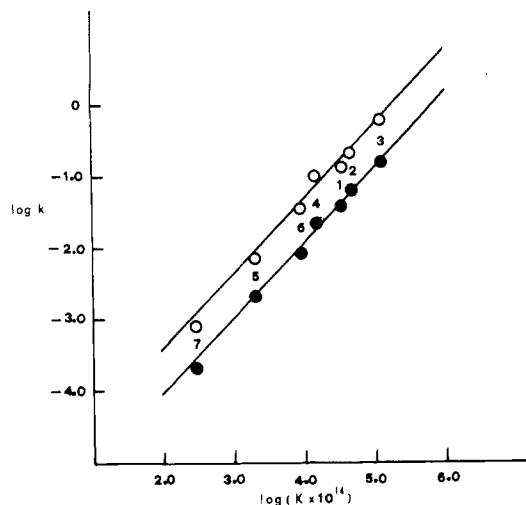


Figure 2. Plots of  $\log k_{25}$  for the reactions of 2- and 3-furoyl chlorides with anilines in benzene against the logarithm of their dissociation constants in water at 25° (Brønsted plots).

Table III  
Infrared Carbonyl Frequencies of the Acid Chlorides in  $\text{CCl}_4$  and  $\log k$  at 25° for the Reaction with Aniline

Acid chloride	Registry no.	$\nu_{\text{C=O}}$ , $\text{cm}^{-1}$	$\log k$
Benzoyl	98-88-4	1777 <sup>a</sup>	-1.2027 <sup>e</sup>
2-Thenoyl	5271-67-0	1753 <sup>b</sup>	-1.5986 <sup>f</sup>
3-Thenoyl	41507-35-1	1766 <sup>c</sup>	-1.3585 <sup>g</sup>
2-Furoyl	527-69-5	1758, 1782 <sup>d</sup>	-0.8761
3-Furoyl	26214-65-3	1765 <sup>c</sup>	-1.3883

<sup>a</sup> C. Garrigou-Lagrange, N. Claveire, J. M. Lebas, and J. M. Jonen, *J. Chim. Phys.*, **58**, 559 (1961). <sup>b</sup> J. J. Peron and P. Saumagne, *Spectrochim. Acta, Part A*, **26**, 1651 (1970). <sup>c</sup> This work. <sup>d</sup> Reference 22. <sup>e</sup> Reference 17. <sup>f</sup> Reference 12. <sup>g</sup> Reference 14.

theoretical line of slope  $-2.303RT$  drawn through the point representing the unsubstituted aniline. The large negative entropies of activation are as expected in reactions involving polar transition states and similar to those found for the 2-<sup>12</sup> and 3-thenoyl<sup>13,14</sup> chloride reactions.

As for the 2-<sup>12</sup> and 3-thenoyl chlorides<sup>14</sup> linear relationships were also found in the reactions of 2- and 3-furoyl chlorides between  $\log k$  at 25° and the  $\text{p}K_a$  values at 25° in water of the corresponding protonated anilines<sup>18</sup> (Figure 2) indicating that the reaction rates of 2- and 3-furoyl chlorides depend on the electron density on the nitrogen atom. The slopes of the Brønsted plots, 1.10 ( $r = 0.997$ ) for 2-furoyl chloride, 1.11 ( $r = 0.997$ ) for 3-furoyl chloride, are similar to those found for the benzoylation, 2-<sup>12</sup> and 3-thenoyl chloride<sup>14</sup> reactions.

The plots of  $\log k$  at 25° for the reactions of 2- and 3-furoyl chlorides against Hammett's  $\sigma$  constants are linear with slopes of  $-3.26$  ( $r = 0.995$ ) and  $-3.28$  ( $r = 0.997$ ) respectively (Figure 3). These values are comparable to those found for benzoylation, 2-<sup>12</sup> and 3-thenoyl chloride<sup>14</sup> reactions.

From these results it is clear that the 2- and 3-furoyl chlorides react with aniline in benzene with the same mechanism as the reaction of benzoylation<sup>19</sup> involving the attack of the lone pair of the electrons of the amino group on the carbonyl carbon atom. The reported results show that the furoyl group functions as electron donating in 3-furoyl chloride and electron withdrawing in the 2-analog relative to the phenyl group in benzoyl chloride. This rate behavior of the 2- and 3-furoyl derivatives has been also noted in the saponification of 2- and 3-furoates.<sup>4-7</sup>

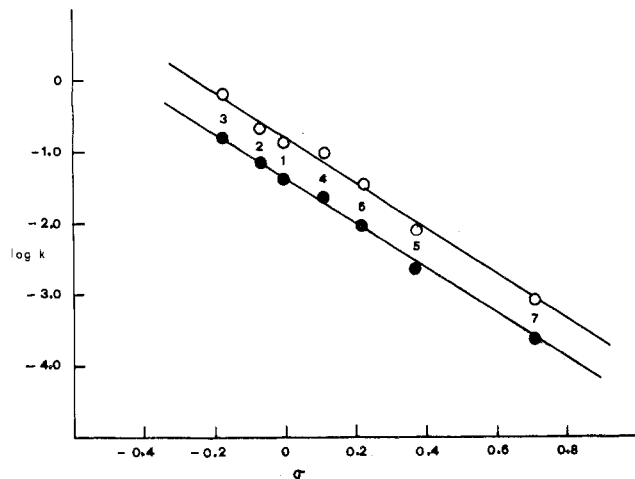


Figure 3. Hammett plots for the reactions of 2- and 3-furoyl chlorides with anilines at 25°.

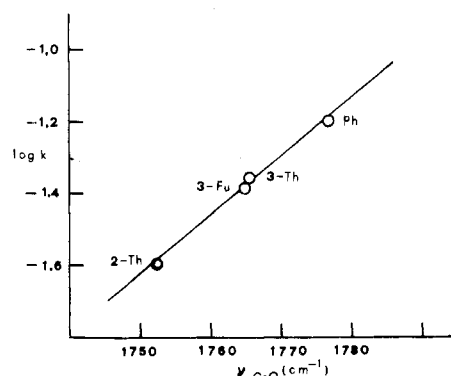


Figure 4. Plots of  $\log k_{25}$  for the reactions of 2-thenoyl, 3-thenoyl, 3-furoyl, and benzoyl chlorides with aniline in benzene against the carbonyl stretching bands in  $\text{CCl}_4$  of the acid chlorides.

Although the infrared carbonyl absorption is property of the ground state only, whereas the reactivity data refer to both reactants and the transition states, a number of examples of linear relationships between the carbonyl stretching bands and the reactivity constants are reported in the literature.<sup>20,21</sup>

In the Table III are listed the  $\log k$  at 25° for the reactions of 2-<sup>12</sup> and 3-thenoyl,<sup>13</sup> 2- and 3-furoyl, and benzoyl chlorides<sup>17</sup> and the infrared carbonyl stretching bands in  $\text{CCl}_4$  of the acid chlorides.

A linear relationship is obtained plotting the  $\log k$  against the carbonyl stretching bands for the reactions of 2- and 3-thenoyl, 3-furoyl, and benzoyl chlorides which demonstrates that the same combination of factors is responsible for both the shift in carbonyl stretching frequency and the reactivity (Figure 4). It is not possible to correlate the  $\log k$  and the carbonyl frequencies of 2-furoyl chloride. In fact in this compound the presence of both s-cis and s-trans rotational isomers has been pointed out.<sup>22,23</sup>

### Experimental Section

**Materials.** The 2- and 3-furoyl chlorides were prepared by refluxing 2 g of 2- or 3-furoic acid (Fluka commercial products) with 10 ml of thionyl chloride for several hours. The excess thionyl chloride was removed by water bath distillation, and the acid chlorides were purified under reduced pressure: 2-furoyl chloride, bp 173–174,<sup>24</sup> 3-furoyl chloride, bp 78–80° (55 mm).<sup>25</sup>

The anilines (Carlo Erba commercial products) were purified to constant melting point or boiling point by recrystallization or fractionation.

The solvent was benzene (R. P. Carlo Erba); no special purification was undertaken.<sup>12</sup>

Table IV  
Physical Constants of 2- and 3-Furanilides<sup>a,b</sup>

No.	X =	Mp, °C	Registry no.	Mp, °C	Registry no.
1	H	124 <sup>e</sup>	1929-89-1	125	52109-86-1
2	<i>m</i> -CH <sub>3</sub>	87 <sup>f</sup>	1982-61-2	117	52109-87-2
3	<i>p</i> -CH <sub>3</sub>	108 <sup>g</sup>	1982-62-3	148	52109-88-3
4	<i>m</i> -CH <sub>3</sub> O	168 <sup>c,h</sup>	52109-84-9	140	52109-89-4
5	<i>m</i> -Cl	116 <sup>i</sup>	2008-49-3	129	52109-90-7
6	<i>p</i> -Cl	146 <sup>i</sup>	1982-59-8	152	52109-91-8
7	<i>m</i> -NO <sub>2</sub>	145 <sup>d,h</sup>	52109-85-0	128	52109-92-9

<sup>a</sup> All the compounds were crystallized from aqueous ethanol. <sup>b</sup> Satisfactory analytical data for N ( $\pm 0.2\%$ ) were reported for 3-furanilides. <sup>c</sup> *Anal.* Calcd for C<sub>12</sub>H<sub>11</sub>NO<sub>3</sub>: N, 6.45. Found: N, 6.41. <sup>d</sup> *Anal.* Calcd for C<sub>11</sub>H<sub>9</sub>N<sub>2</sub>O<sub>4</sub>: N, 12.06. Found: N, 11.95. <sup>e</sup> P. Grammaticakis, *Bull. Soc. Chim. Fr.*, 979 (1948). <sup>f</sup> J. Heilbron and H. M. Bumbury, "Dictionary of Organic Compounds," p 560, Eyre and Spottiwode (1946). <sup>g</sup> C. Tsuchiya, *Nippon Kagaku Zasshi*, **82**, 1395 (1961); *Chem. Abstr.*, **59**, 2751 (1963). <sup>h</sup> This work. <sup>i</sup> Buu-Hoi and Ngugen Hoan, *Recl. Trav. Chim. Pays-Bas*, **68**, 5 (1949).

**Infrared Spectra.** Spectra of 3-thenoyl<sup>14</sup> and 3-furoyl chlorides were measured on a Hitachi Perkin-Elmer EPS-3T spectrometer using cell of 0.1 mm thickness. The solvent was CCl<sub>4</sub> of spectroscopic grade. In Table III are listed the infrared carbonyl bands of the acid chlorides.

**Kinetic Procedure.** The reactions were followed kinetically, as previously,<sup>14</sup> by filtering the completely insoluble aniline hydrochloride, dissolving it in water, and estimating the chloride with 0.01 mercury(II) nitrate, using diphenylcarbazone as indicator, in the presence of bromophenol blue.

The second-order rate constants were derived from the formula

$$k_2 = \frac{1}{2 \times 60t} \left( \frac{1}{100 - X} - \frac{1}{100} \right) \frac{100}{a}$$

where  $t$  is the time in minutes,  $X$  is the percentage change,  $k_2$  is the velocity constant (liters/mole seconds), and  $a$  is the initial concentration of the acid chloride in moles/liter.<sup>14</sup>

The second-order rate constants were calculated with constant molar ratios of the reactants (1:2): 1 mol of acid chloride with 2 mol of aniline, in agreement with eq 1. For the 2-furoyl chloride reaction and compounds no. 2 and 3 for the 3-furoyl chloride reaction the initial concentration of the reactants after mixing were acid chloride 0.0025 *M*, aniline 0.005 *M*. For other compounds in Table II the initial concentrations were 0.005 *M* 3-furoyl chloride and 0.01 *M* aniline.

All compounds gave excellent second-order kinetics. All rates were run in duplicate to the least 80% completion with less than 3% deviation between the two rate constants. At temperatures other than 15 or 25°, rate coefficients were corrected for thermal expansion or contraction of the solvent. All rate constants were calculated by a least-squares computer program with a Hewlett-Packard 9100 B. The activation parameters were calculated from a least-squares treatment of  $\log k$  against  $T^{-1}$ . The estimated precision is ca.  $\pm 0.5$  kcal mol<sup>-1</sup> in  $E_A$  and  $\pm 2$  cal mol<sup>-1</sup> °K<sup>-1</sup> in  $\Delta S^\ddagger$ .

**Product Analysis.** Standard solutions of the appropriate aniline and 2- or 3-furoyl chloride in benzene were placed in a glass-stoppered bottle and maintained at the kinetic temperature until completion. After concentration of the benzenic solution to small volume, the 2- or 3-furanilide was filtered, washed free from aniline hydrochloride with water, dried, and recrystallized from aqueous ethanol.

In all cases the amount of the furoanilide was  $\geq 95\%$  of that ex-

pected from the formation of 1 mol of anilide per mol of acid chloride consumed. Physical constants and analytical data of furanilides are reported in Table IV.

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