

## FUROYLATION OF ALKYLBENZENES

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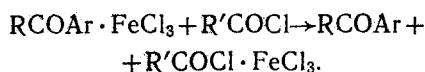
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The acylation of alkylbenzenes with furoyl chloride in the presence of catalytic amounts of  $\text{FeCl}_3$  requires a relatively high reaction temperature ( $150^\circ\text{C}$ ) and is accompanied by the elimination of alkyl groups. It is shown by the method of competitive reactions of furoyl and benzoyl chlorides with aromatic compounds that the activity of furoyl chloride is higher when small amounts of the catalyst are present.

Furyl aryl ketones are usually obtained by acylation of aromatic hydrocarbons with 2-furoyl chloride in the presence of 1-2 moles of aluminum chloride or stannic chlorides [1, 2]. The synthesis of these ketones can also be carried out in the presence of  $10^{-2}$ - $10^{-3}$  mole of ferric chloride [3], and the yields in the case of high-boiling aromatic compounds (anisole, xylene, and mesitylene) reach [3] 85%, whereas the temperature of refluxing toluene is insufficient for a complete reaction (the yield of ketone is 28%). In fact, we have shown that heating of a mixture of ethylbenzene, 2-furoyl chloride, and ferric chloride in a ratio of 3:1: $10^{-3}$  gives 45% of a ketone fraction as compared with up to 58% of a mixture of ketones in the case of n-propyl- and isopropylbenzenes, and up to 80% of the corresponding ketone in the case of n- and tert-butylbenzenes. The maximum yield is obtained when the reaction mixture is heated for 5 h, although the bulk of the product is formed in the first hour.

According to the results of gas-liquid chromatography (GLC), primarily 4-aryl furyl ketones are formed (85-94%). It was found that partial splitting out of the alkyl groups occurs under the reaction conditions, and lower-molecular-weight ketones up to phenyl furyl ketone are formed in up to 7% yields (Table 1). The formation of phenyl furyl ketone is particularly appreciable in the furoylation of isopropyl- and tert-butylbenzenes. It has been reported that only 4-aryl furyl ketones are isolated in the presence of aluminum chloride [4]. We have shown that elimination of hydrocarbon radicals also occurs in the presence of  $\text{AlCl}_3$  (Table 1).

According to the results of the experiments of various authors, who carried out the reaction both in the presence of equimolar amounts of aluminum chloride [5] and in the presence of  $10^{-3}$ - $10^{-4}$  mole of ferric chloride [6], it is impossible to determine the relative activities of furoyl and benzoyl chlorides. We used a method that has been successfully used for the determination of the relative activities of substituted benzoyl chlorides [7], viz., the competitive reactions of 2-furoyl and benzoyl chlorides with anisole and mesitylene in the presence of catalytic amounts of ferric chloride. It is apparent from Table 2 that the relative activities of the acyl halides are virtually independent of the amount of aromatic compound and that in all cases 2-furoyl chloride is more active than benzoyl chloride by a factor of 1.3. Similar data were also obtained in experiments with mesitylene (Table 2). The possibility of the use of small amounts of the catalyst is due to the occurrence of an exchange process [8]:



Since the yield of the corresponding ketone depends on the basicity of the carbonyl oxygen atom of the acyl halide, 2-furoyl chloride, which is the more basic acyl halide, forms a more reactive complex and gives higher yields of the furoyl ketones. According to the data

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TABLE 1. Furoylation of Alkylbenzenes  $C_6H_5R$ 

R	Catalyst	Reaction temp., °C	Time, h	Overall yield, %	Phenyl furyl ketone, %	4-Aryl furyl ketone, %	Unidentified impurities, %
$C_2H_5$	$FeCl_3$	130—140	5	45	3	93	4
$C_2H_5$	$AlCl_3$	25	1	80	2	93	5
$n-C_3H_7$	$FeCl_3$	160—165	5	58	3	94	3
$n-C_3H_7$	$AlCl_3$	25	1	80	2	94	4
$i-C_3H_7$	$FeCl_3$	155—160	5	57	5	90	5
$i-C_3H_7$	$AlCl_3$	25	1	81	4	91	5
$n-C_4H_9$	$FeCl_3$	170—180	5	80	5	90	5
$n-C_4H_9$	$AlCl_3$	25	1	82	4	90	6
$t-C_4H_9$	$FeCl_3$	170—180	5	76	7	86	7
$t-C_4H_9$	$AlCl_3$	25	1	78	6	85	9

TABLE 2. Competitive Reactions of 2-Furoyl and Benzoyl Chlorides in the Presence of Ferric Chloride (at 155°C for 3 h)

Hydrocarbon:2-furoyl chloride:benzoyl chloride:ferric chloride molar ratios	Yield of product according to GLC, %	
	Furoylation	Benzoylation
Anisole		
10:1:1:1.4·10 <sup>-2</sup>	65	48
5:1:1:1.4·10 <sup>-2</sup>	68	54
1:1:1:1.4·10 <sup>-2</sup>	48	37
Mesitylene		
12:1:1:1.2·10 <sup>-2</sup>	71	58
6:1:1:1.2·10 <sup>-2</sup>	63	52
1:1:1:1.2·10 <sup>-2</sup>	52	44

in [9], other factors (e.g., the electrophilicity of the carbon atom of the carbonyl group and the strength of the C—Cl bond) play an insignificant role. Similarly, when 1 mole of aluminum chloride per 2 moles of a mixture of the same acyl chlorides is used, the yield of the furyl ketone is higher by a factor of 1.15, although more of the phenyl ketone is formed in the case of excess catalyst (2.4 moles per 2 moles of the mixture of acyl chlorides) because of the higher reactivity of the less stable complex of benzoyl chloride with aluminum chloride.

The results obtained with  $FeCl_3$  are consequently characteristic only for those acylation reactions that are carried out in the presence of small amounts of the catalysts, since 81% furoylanisole and 83% 4-methoxybenzophenone are obtained when each of these reactions is carried out separately under identical conditions at an anisole:acyl chloride: $FeCl_3$  molar ratio of 5:1:1.2·10<sup>-2</sup>. Thus, no difference in the reactivities of 2-furoyl and benzoyl chlorides is manifested under these conditions.

## EXPERIMENTAL

Chromatography was carried out with a Tsvet-1-64 chromatograph with a 2000 × 4 mm steel column filled with 10% Apiezon L on cellite, the carrier gas was hydrogen, the flow rate was 30 ml/min, and the temperature was 265°C.

The experiments with aluminum chloride were carried out by the following general method. A 0.05-mole sample of aluminum chloride was added to a mixture of 0.15 mole of monoalkylbenzene and 0.05 mole of 2-furoyl chloride, and the product was isolated by the usual workup after the mixture was stirred for 1 h. A mixture of 16.5 g (0.15 mole) of ethylbenzene, 6.5 g (0.05 mole) of 2-furoyl chloride, and 0.1 g of ferric chloride was heated at the boiling point for 5 h, after which 20 ml of methanol was added to the mixture to tie up the residual 2-furoyl chloride, and the mixture was heated for another 30 min. Fractionation then yielded 4.5 g (45%) of a ketone fraction with bp 136–138°C (5 mm) (bp 128–130°C (2 mm) [4]).

The following compounds were similarly obtained: p-propylphenyl 2-furyl ketone with bp 139-141°C (5 mm) and mp 48°C (mp 48°C [2]), p-isopropylphenyl 2-furyl ketone with bp 140-141°C (5 mm) and mp 50°C (mp 50-51°C [4]), p-tert-butylphenyl 2-furyl ketone with bp 146-148°C (5 mm) and mp 59°C (mp 58-59°C [4]), and p-butylphenyl 2-furyl ketone with bp 147-149°C (5 mm) and mp 65°C. Found: C 78.8; H 6.9%; C<sub>15</sub>H<sub>16</sub>O<sub>2</sub>. Calculated: C 78.9; H 7.0%.

The competitive reactions were carried out by the following method. A mixture of 0.05 mole of anisole (or mesitylene), 0.05 mole of 2-furoyl chloride, 0.05 mole of benzoyl chloride, and 0.1 g of ferric chloride was heated at 155°C for 3 h, after which 10 ml of alkali was added to tie up the acyl chloride residues, and the mixture was extracted with benzene. The solvent was removed by distillation, and the residue was distilled in vacuo. A fraction with bp 145-155°C (3 mm) was isolated in the experiment with mesitylene, and a fraction with bp 160-190°C (3 mm) was isolated in the experiment with anisole.

The yields of the products were determined by using p-furoylanisole and 2,4,6-trimethylphenyl furyl ketone as internal standards.

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#### SYNTHESIS OF 4-OXO-1,3-BENZ- AND NAPHTHOXAZINIUM SALTS FROM o-HYDROXYARYLAMIDES

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The acid-catalyzed acylation of primary and secondary o-hydroxyaryl amides, the probable reaction scheme, and the possibility of the formation of 4-oxo-1,3-arenoxazinium salts and analogs in the reaction of amides of salicylic, coumaric, and 1-hydroxy- and 3-hydroxynaphthoic acids and their N-alkyl(aryl) derivatives with excess amounts of aliphatic acid anhydrides and 70% perchloric acid, as well as by the acid cyclization of O- and N-mono- and diacyl derivatives of these amides, are examined. Twelve previously unknown 2-alkyl- and 2-styryl-4-oxo-1,3-naphth[3,2-e]- and -[1,2-e]oxazinium perchlorates were synthesized. N-Methyl- and N-benzylamides of 8-acetoxy-1-naphthoic acid are formed instead of the expected peri-cyclic analogs of oxazinium salts in the reaction of 8-hydroxy-1-naphthoic acid anilides with acetic anhydride and perchloric acid.

The reaction of salicylamide and N-substituted salicylamides with alkanecarboxylic acids and perchloric acid leads to the production of 4-oxo-1,3-benzoxazinium perchlorates [1]. To ascertain the effect of benzo annelation on the stabilities and properties of 4-oxo-1,3-oxazinium cations in the present research we used the same method for the preparation of a number of previously unknown 2-alkyl-4-oxo-1,3-naphth[3,2-e]- and -[1,2-e]oxazinium salts (I, II). The synthesized naphthoxazinium perchlorates (I-II) are less stable than

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