The Mechanism of Fries Rearrangement and Acylation Reaction in Polyphosphoric Acid

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Acylation reaction of *m*-cresol with 2-chlorobenzoic acid in PPA occurred through a prior esterification, followed by a Fries rearrangement of ester (**3**) to give benzophenones **4**—**7**.

Ester **3** undergoes the Fries rearrangement in PPA, giving benzophenones **4**—**7** in about the same yield as can be obtained by direct acylation reaction of *m*-cresol with 2-chlorobenzoic acid. The benzophenone **5** is not stable in PPA and decomposed to benzophenone (**4**). The formation of benzophenones **4**—**7**, from Fries rearrangement of the ester **3** was interpreted by an intermolecular mechanism.

Gardner[1] and Snyder and Elston[2] have reported that polyphosphoric acid (PPA) as a reaction medium and a catalyst can convert phenyl benzoate, depending on the conditions, to 4-hydroxybenzophenone in poor yield, or this same phenol in higher yield, and the keto ester (**10**). Condensation of phenol and benzoic acid in this medium resulted in trace amounts of phenyl benzoate, and appreciable quantities of 4-hydroxybenzophenone have been formed in rearrangement and acylation reactions in polyphosphoric acid.[3—5] (Chart 1.)

The mechanisms of Fries rearrangements and acylation reactions in PPA are not discussed in detail, and the relationship between the rearrangement and acylation reactions under the selected conditions in PPA is not established. In this paper we wish to report PPA to be as a novel, mild and efficient reagent capable of achieving Fries rearrangement in general, and to afford unpredictable products in some particular cases. The suggested mechanism for the aforementioned reaction in PPA using, the effect of temperature, and the effect of time are discussed in detail.

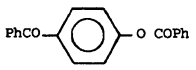

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Chart 1.

Results and Discussion

M.J.S. Dewar[6] has reported that the acylation reaction with $AlCl_3$, gives the hydroxybenzophenones entirely through a prior esterification process, followed by a rearrangement reaction. In an attempt to determine whether this was the only mode of formation of the hydroxybenzophenones in PPA, the acylation reaction of *o*-chlorobenzoic acid (**1**) and *m*-cresol (**2**) was investigated.

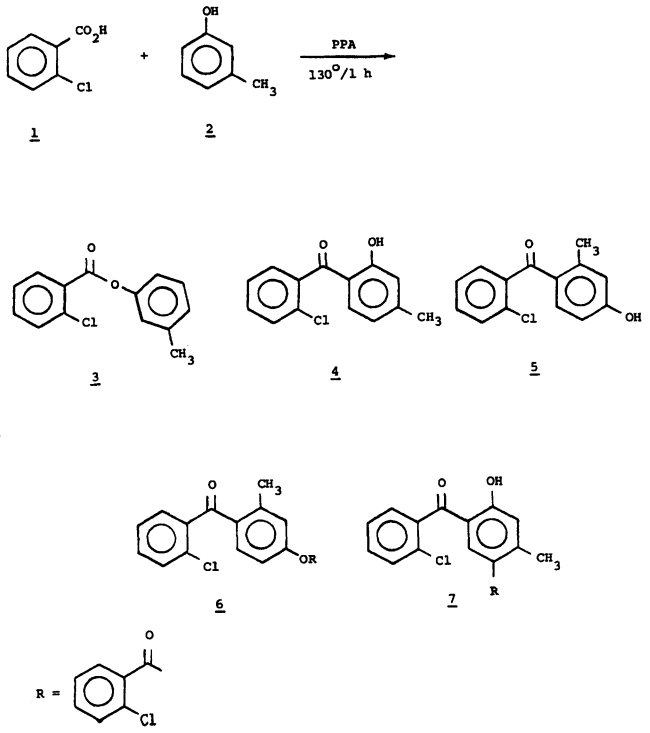
Acylation reaction of *o*-chlorobenzoic acid (**1**) with *m*-cresol (**2**) in PPA was achieved at 130°C for 1h, and 3-methylphenyl 2-chlorobenzoate (**3**), 2′-chloro-2-hydroxy-4-methylbenzophenone (**4**), 2′-chloro-4-hydroxy-2-methylbenzophenone (**5**), 2′-chloro-4-(2-chlorobenzoyloxy)-2-methylbenzophenone (**6**), and 2,4-bis(2-chlorobenzoyl)-5-methylphenol (**7**) were formed (Scheme 1, Table 1).

Having this information, the above reaction was carried out at different conditions and the reactions were monitored by ^{1}H NMR spectroscopy. The results are summarized in Table 1, which clearly indicate the following points.

1. Ester **3** is formed first, and then decomposed in the course of the reactions. It should be noted that increasing the temperature affected the decomposition rate of reactions.
2. The product **4** was formed in the course of the reactions and the rate of its formation increased with increasing the temperature.
3. The products **5** and **6** were formed when the reactions were carried out at 25, 70, and 90°C. However **5** and **6** were decomposed gradually at the range of 110—130°C.
4. At the begining of the reactions, the mol% of products **5** and **6** were more than mol% of product **4** while prolonging the reaction time and raising the temperature result in disappearance of **5** and **6**, and increment in the mol% of **4**.
5. The product **7** was only formed at 130°C.

In all cases ester **3** was formed. However, by increasing temperature and time, this ester was found to be decomposed. Therefore, we expect that acylation reaction occurs through a prior esterification, followed by rearrangement. To examine our speculation the following experiments were carried out.

The ester **3** was treated with PPA at 70 and 130°C and the results are collected in Table 2. According to Table 2 it was established that progress of the reaction of the ester **3** was similar to that of the reaction of *o*-chlorobenzoic acid (**1**) and *m*-cresol (**2**) in the presence of PPA. From the observed experimental data we concluded that Fries rearrangement has occurred in these reactions. It should be noted that ester **3** in the absence of PPA did not afford the rearranged products and only the starting material was recovered.



Scheme 1.

Three mechanistic pathways are proposed in the literature for Fries rearrangement; (a) intramolecular,[6—14] (b) bimolecular,[6,11,14—19] and (c) intermolecular.[19—27] In the intramolecular rearrangement, acyl group shifts directly from oxygen atom to the carbon atom of the ring. In the bimolecular pathway, it is proposed that one molecule of the phenyl ester is acylated by another molecule. In the intermolecular mechanism, the ester is assumed to react with Lewis acid to give an oxocarbonium ion and a phenol which combine to form a derivative of the hydroxyketone.

Based on the aforementioned mechanisms and our observatioins the following mechanisms are suggested (Scheme 2).

As it is seen Scheme 2 clearly suggests the following possibilities:

1. The compound **4** can be obtained from the intramolecular rearrangement of ester **3** and also by the rearrangement of compound **5** (Gore's reversibility concept.[5,28—34])
2. The compound **5** can be obtained from the intermolecular rearrangement of ester **3** and also by the trans esterification of compound **6**.
3. The compound **6** can be obtained from the esterification of compound **5** and also by the bimolecular rearrangement of ester **3**.
4. The compound **7** can be obtained from the electrophilic aromatic substitution of compounds **4** and **5** and also directly from the rearrangement of compound **6**.

Table 1. The Reaction of *o*-Chlorobenzoic Acid (**1**) with *m*-Cresol (**2**) in PPA

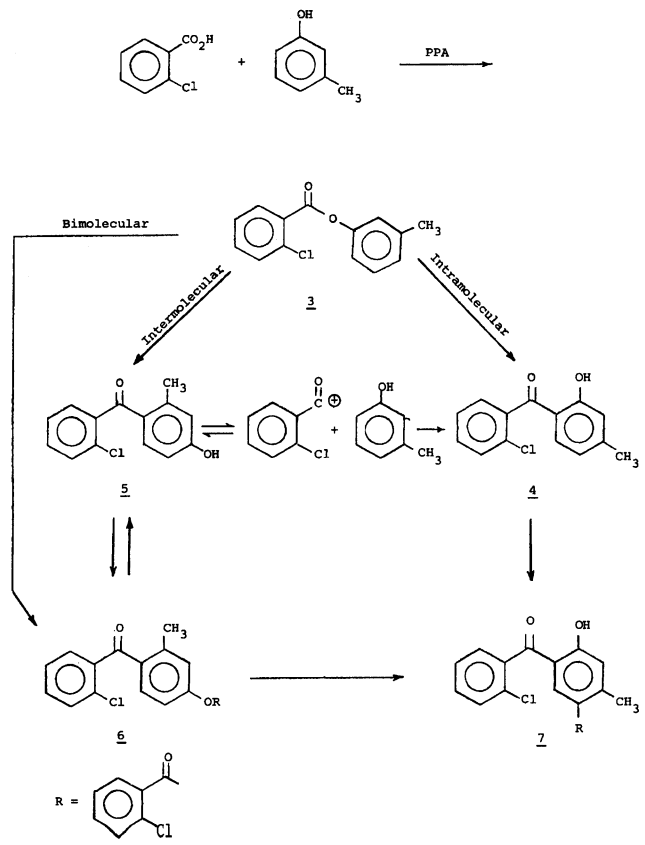
Time/min	Temp/°C	Yield/% [a]					
		2	**3**	**4**	**5**	**6**	**7**
360	25	12	47.3	6	2.8	31.7	—
2160	25	5	37.5	12.5	13.8	31.2	—
43200	25	4	31	13.5	9	42	—
10	70	77	17	—	6	—	—
20	70	49	36	—	15	—	—
30	70	12	53	—	14.5	20.5	—
45	70	4.5	46.5	6.5	16	26.5	—
60	70	—	42	10.5	18.5	29	—
240	70	—	25	14.5	24.5	36	—
10	90	2.5	48	13	17.5	19	—
20	90	1.5	32	14	25.6	25.6	—
30	90	1.5	26	15.5	30	27	—
40	90	—	22	19.5	30.5	28	—
60	90	—	18.5	22	31	28.5	—
10	110	4.3	27.5	20.7	26.5	21	—
20	110	4	19.5	23	28.5	25	—
30	110	—	16.5	27.5	29.5	26	—
40	110	—	13	34	28	25	—
60	110	—	9.5	50	21	19.5	—
240	110	—	—	77.5	9	13.5	—
10	130	5.3	19.5	25.5	21.5	28	—
20	130	5.5	14	42	13	20	5.5
30	130	5.5	10	53.5	10.5	14	5.6
40	130	5.5	7	63	8	9.5	7
60	130	5.5	4	72	4.5	5	10
90	130	4	3	73	4	3.5	12.5
120	130	4	—	75	3	3	15

a) The results are average values calculated from the results of several experiments and yields are shown as mole percent that calculated from ^{1}H NMR spectra.

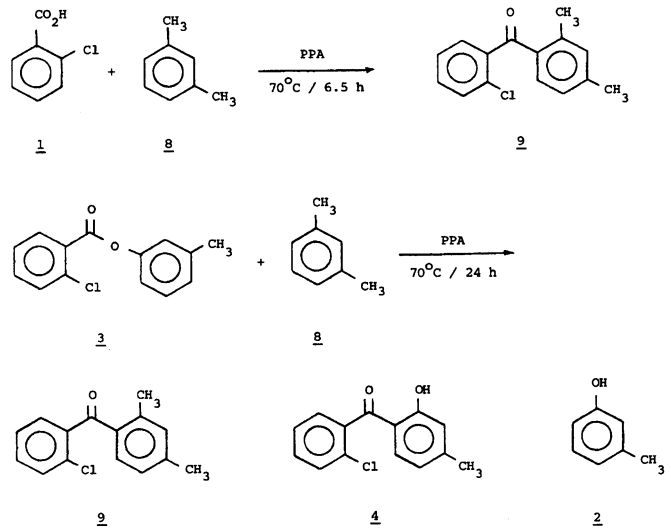
Table 2. Progress of Fries Rearrangement of Ester **3**

Time/min	Temp/°C	Yield/%				
		3	**4**	**5**	**6**	**7**
60	70	77.5	6	13	3.5	—
120	70	69	8	16.5	6.5	—
180	70	57	9.5	23	10.5	—
240	70	39	11	33	17	—
360	70	18	16	42	24	—
1800	70	—	60	16	16	8
10	130	38.4	49	5	7.6	—
20	130	12	71	4	8.4	4.6
30	130	6.5	80	1.5	5	7
40	130	—	87	—	3.7	9.3
60	130	—	84	—	—	16

In a separate experiment, when compound **5** was added to PPA and stirred for 24 h at 70°C, the compounds **4** and **7** were formed in the ratio of 4 : 1 respectively. These results exhibited that the conversion of compound **5** to compound **4** occurred with decomposition of compound **5** to *m*-cresol (**2**) and oxocarbonium ion followed by reformation to compound **4** (Gore's reversibility concept[5,28—34]). When compound **4** was treated with PPA at 130°C for 6 h, the compound **7**



Scheme 2.



Scheme 3.

Table 3. Progress of Fries Rearrangement of Ester **3** in the Presence of *m*-Xylene

Time/h	Temp/°C	Yield/%		
		3	**4**	**9**
1	70	83	—	17
2	70	82	—	18
6	70	75	5	20
24	70	28	12	50

was formed in 14% yield.

These results clearly indicate that the compound **4** can be obtained from rearrangement of compound **5**, but still some of the compound **4** may be also obtained from intramolecular rearrangement of ester **3**. If an oxocarbonium ion, in the presence of PPA, is free, it could be trapped by an acyl acceptor. Such an acceptor ought to afford product(s) that would readily be confirmed from the normal products of a Fries rearrangement. One experiment was devised to test this supposition, *o*-chlorobenzoic acid (1) being allowed to react with *m*-xylene (**8**) in the presence of PPA. From the reaction mixture of *o*-chlorobenzoic acid (**1**) and *m*-xylene (**8**) at 70°C after 6.5 h, 2′-chloro-2,4-dimethylbenzophenone (**9**) was isolated in 79% yield (Scheme 3). It is evident that *m*-xylene (**8**) ring attacked oxocarbonium ion readily. Therefore *m*-xylene (**8**) which was found to be an effective competitor, was selected and ester **3** was reacted with 2.5 equivalent of *m*-xylene (**8**) at 70°C in the presence of PPA (Scheme 3). The competitive Fries reaction which results are shown in Table 3, showed that after 2 h Fries rearrangement products was not formed and only compound **9** was obtained.

Thus we had expected to obtain an equilibrium by extending the time of the reaction from 2 to 24 h that only 12% of compound **4** was formed, which was rather poor and reasonable, because the *m*-cresol (**2**) ring also is reactive such as *m*-xylene (**8**) ring. Considering the above discussion and the fact that the compound **6** was not formed during these competitive reactions, it can be safely concluded that the formation of hydroxybenzophenones from Fries rearrangement of ester **3** occurs via an intermolecular mechanism.

Experimental

Solvents, reagents, and chemical materials were obtained from Merck Chemical Company (West Germany) and Fluka (Switzerland). Melting points were determined in open capillary tubes in a Buchi 510 circulating oil melting point apparatus and uncorrected. IR spectra were recorded on a Perkin Elmer 157G and 781 spectrophotometers. ^{1}H NMR spectra were obatained on a Hitachi R-248 (60 MHz) for solutions in $CDCl_3$ with tetramethylsilane as internal standard. Mass spectra were determined on a varian CH-5 or varian Mat-112 at 70 eV. UV spectra were recorded on a cary 118 UV instrument. Thin-layer chromatography were carried out on silica gel 60F 254 analytical sheets obtained from Merck Chemical Company (West Germany). Column chromatography was carried out on the short column of silica gel 60 Merck (230—400 mesh) in glass columns (ϕ 2 or 3 cm) using 15—30 g of silica gel per one gram of crude mixture.

General Procedure for the Fries Rearrangement. Representative Procedure: A mixture of *o*-chlorobenzoic acid (0.01 mol, 1.56 g) and *m*-cresol (0.01 mol, 1 ml) was added to PPA (freshly prepared from 5 ml of H_3PO_4 and 8 g of P_2O_5), and heated with stirring at 130°C for 1 h, then poured into cold water. Extracted with chloroform (200

ml) and washed with sodium hydrogencarbonate solution (2×150 ml), dried with calcium chloride and evaporated. Resulted mixture was chromatographed over silica gel. Elution with CCl_4 gave 3-methylphenyl 2-chlorobenzoate (**3**) (90 mg) as golden viscous oil (lit,[35] bp 198°C/2.5 mmHg) (1 mmHg=133.322 Pa), and 2′-chloro-4-(2-chlorobenzoyloxy)-2-mthylbenzophenone (**6**) (180 mg) as golden viscous oil respectively, and the CCl_4-$CHCl_3$ (1:1) elution gave 2′-chloro-2-hydroxy-4-methylbenzophenone (**4**) (1 g) as white needles, mp 106°C (lit,[35] 106°C), 2, 4-bis(2-chlorobenzoyl)-5-methylphenol (**7**) (200 mg) as white crystals, mp 105—107°C, and 2′-chloro-4-hydroxy-2--methylbenzophenone (**5**) (100 mg) as white crystals, mp 153°C (lit,[35] 159, lit,[36] 153°C) respectively. Further elution with $CHCl_3$-CH_3OH (5:1) fraction furnished *m*-cresol (60 mg).

3-Methylphenyl 2-Chlorobenzoate (3) ^{1}H NMR ($CDCl_3$) δ=2.3 (s, 3H, CH_3), 6.8—7.5 (complex, 7H), 7.9 (dd, 1H, J=7 and 2 Hz).

2′-Chloro-2-hydroxy-4-methylbenzophenone (4). ^{1}H NMR ($CDCl_3$) δ=2.3 (s, 3H, CH_3), 6.5 (d, 1H, J=8 Hz), 6.75 (s, 1H), 7.0 (d, 1H, J=8 Hz), 7.15—7.45 (unresolved, 4H), 12 (s, 1H, OH); IR (KBr) 3300—2700(b), 1635(s), 1610(s), 1505(m), 1475(m), 1435(s), 1335(s), 1310(m), 1250(m), 1055(m), 1035(w), 915(m), 765(s), 615(m); UV ($CHCl_3$) λ_{max} 273 nm.

2′-Chloro-4-hydroxy-2-methylbenzophenone (5). ^{1}H NMR ($CDCl_3$) δ=2.5 (s, 3H, CH_3), 6.5 (d, 1H, J=8 Hz), 6.55 (d, 1H, J=8 Hz), 6.65 (s, 1H), 7.0—7.5 (complex, 5H); IR (KBr) 3360(b), 1640(s), 1620(m), 1560(s), 1430(m), 1290(s), 1235(s), 1115(m), 1050(m), 765(m), 620(m); UV ($CHCl_3$) λ_{max} 285 nm.

2′-Chloro-4-(2-chlorobenzoyloxy)-2-methylbenzophenone (6). (Found: C, 65.3; H, 3.7%. Calcd for $C_{21}H_{14}O_3Cl_2$: C, 65.5; H, 3.6%). ^{1}H NMR ($CDCl_3$) δ=2.56 (s, 3H, CH_3), 6.85—7.6 (complex, 10 H), 8.0 (dd, J=6 and 2 Hz); IR (KBr) 3070(w), 2975(w), 2925(w), 1750(s), 1670(s), 1590(s), 1435(s), 1240(s), 1220(s), 1160(m), 1115(m), 1035(s), 960(m), 905(m), 740(s), 665(m); UV ($CHCl_3$) λ_{max} 267 nm.

2, 4- Bis(2- chlorobenzoyl)- 5- methylphenol (7). (Found: C, 65.7; H, 3.8%. Calcd for $C_{21}H_{14}O_3Cl_2$: C, 65.5; H, 3.6%). ^{1}H NMR ($CDCl_3$) δ=2.6 (s, 3H, CH_3), 6.9 (s, 1H), 7—7.5 (complex, 10H), 12.2 (s, 1H, OH); IR (KBr) 3500—2800 (w), 1640(s), 1630(s), 1565(s), 1435(s), 1295(s), 1240(s), 1100(s), 750(s).

Fries rearrangement was carried out at 25, 70, 90, 110, and 130°C with above procedure and worked up at different time (Table 1). This reaction was also carried out at different equivalent of PPA (1—6 equivalent) at 70°C for 6.5 h. The results which are given below (Table 4) were calculated from NMR spectrums of the reaction mixtures.

3-Methylphenyl 2-Chlorobenzoate (3). To a stirred solution of *m*-cresol (0.01 mol, 1 ml) in an aqueous 10% sodium hydroxide (15 ml), was injected 2-chlorobenzoyl chloride (2.685 g, 1.83 ml, 0.015 mol) and stirred for 20 min at room temperature. Extracted with ethyl acetate (200 ml) and washed with sodium hydrogencarbonate solution (2×150 ml), water (100 ml) and dried ($CaCl_2$). The solvent evaporated to give 3-methylphenyl 2-chlorobenzoate (**3**) (2.34 g, 95%) as a golden vicious oil. ^{1}H NMR ($CDCl_3$) δ=2.3 (s, 3H, CH_3), 6.8—7.5 (m, 7H), 7.9 (dd, 1H, J=7 and 2 Hz, 6-H).

Table 4.

PPA/*o*-Chlorobenzoic acid	Yield %				
	3	**4**	**5**	**6**	**7**
1	62	17	5.5	8	7.5
2	44	17.5	16	22.5	0
3	28	32	14	26	0
6	9.0	27		64	

Fries Rearrangement of 3-Methylphenyl 2-Chlorobenzoate (3). 3-Methylphenyl 2-chlorobenzoate (**3**) (2.465 g, 0.01 mol) was added to PPA (freshly prepared from 5 ml of H_3PO_4 and 8 g of P_2O_5) heated with stirring at 70°C for 30 h. At different times the reaction mixture was poured into cold water. Extracted with chloroform (200 ml), washed with sodium hydrogencarbonate solution (150 ml) and water (100 ml). The organic layer was dried ($CaCl_2$) and evaporated (Table 2).

Condensation of *o*-Chlorobenzoic Acid and *m*-Xylene. A mixture of phosphorus pentaoxide P_2O_5 (8 g) and phosphoric acid (5 ml) was heated on an oil bath until a clear solution was obtained. A mixture of *o*-chlorobenzoic acid (0.01 mol, 1.56 g) and *m*-xylene (0.01 mol, 1.25 ml) was added to freshly prepared PPA. The reaction mixture was heated at 70°C for 6.5 h. Then the mixture was poured into cold water (200 ml), extracted with ethyl acetate (200 ml) and washed with sodium hydrogencarbonate solution (2×100 ml) and water (100 ml), dried with calcium chloride and evaporated. 2′-Chloro-2,4-dimethylbenzophenone (**9**) was obtained (1.79 g, 79%) as an yellow oil. ^{1}H NMR ($CDCl_3$) δ=2.3 (s, 3H, CH_3), 2.55 (s, 3H, CH_3), 6.7—7.3 (complex, 7H); IR (neat) 1660(s), 1600(s), 1430(s), 1230(s) 1120(m), 1030(m), 890(m), 740(s).

Fries Rearrangement of 3-Methylphenyl 2-Chlorobenzoate (3) in the Presence of *m*-Xylene. A mixture of 3-methylphenyl 2-chlorobenzoate (**3**) (0.01 mol, 2.465 g) and *m*-xylene (0.025 mol, 2.654 g, 3.1 ml) was added to PPA (freshly prepared from 5 ml H_3PO_4 and 8 g of P_2O_5) and heated with stirring around 70°C for 24 h, and then poured into cold water. Extracted with chloroform (200 ml), and washed with sodium hydrogencarbonate solution (2×150 ml), water (100 ml), dried over calcium chloride, and evaporated (Table 3).

Isomerization of 2′-Chloro-4-hydroxy-2-methylbenzophenone (5) in Polyphosphoric Acid. A mixture of 4 g of P_2O_5, 2.5 ml of H_3PO_4 and 2′-chloro-4-hydroxy-2-methylbenzophenone (**5**) (0.001 mol, 250 mg) was heated and stirred at 130°C for 4 h. The mixture, was poured into cold water and extracted with ethyl acetate (200 ml) and washed with water. Organic layer dried with calcium chloride and evaporated. NMR-spectrum of the resulted mixture (150 mg) showed that 15% of 2,4-bis(2-chlorobenzoyl)-5-mehtylphenol (**7**), and 2′-chloro-2-hydroxy-4-methylbenzophenone (**4**) (60%) were formed.

Isomerization of 2′-Chloro-2-hydroxy-4-methylbenzophenone (4) in Polyphosphoric Acid. A mixture of 4 g of P_2O_5, 2.5 ml of H_3PO_4, and 2′-chloro-2-hydroxy-4-methylbenzophenone (**4**) (0.001 mol, 250 mg) was heated and stirred at 130°C for 6 h. The mixture was poured into cold water and extracted with ethyl acetate (200 ml) and washed with water. Organic layer dried with calcium

chloride and evaporated. NMR-spectrum of the resulted mixture (150 mg) was showed that 54% starting material, 14% of 2,4-bis(2-chlorobenzoyl)-5-methylphenol (**7**), and 32% of *m*-cresol are present.

2,4-Bis(2-chlorobenzoyl)-5-methylphenol (7). A mixture of 2′-chloro-2-hydroxy-4-methylbenzophenone (**4**) (0.005 mol, 1.2 g) and *o*-chlorobenzoic acid (0.005 mol, 0.8 g) was added to PPA (freshly prepared from 8 g of P_2O_5 and 5 ml of H_3PO_4). The mixture was heated and stirred at 70°C for 20 h. The reaction mixture was poured into cold water and extracted with chloroform (2×100 ml) and washed with water (100 ml), sodium hydrogencarbonate (2×100 ml), dried with calcium chloride and evaporated. The resulted mixture (1.46 g, 76%) was recrystalized from hexane and the 2,4-bis(2-chlorobenzoyl)-5-methylphenol (**7**) was obtained as white crystals, mp 105—107°C.

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