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$AlCl_3$-Catalyzed Reaction of Benzene with Homophthalic Anhydride

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The $AlCl_3$-catalyzed acylation of benzene with homophthalic anhydride was carried out under various conditions. A mixture of 2-benzoylphenylacetic acid (**2**), 2-phenacylbenzoic acid (**3**) and isobenzalphthalide (**4**) was obtained. The reaction pathway of the products was also discussed in the present work.

Although homophthalic anhydride (**1**) has been widely used as a starting materials in a field of organic synthesis,[1-2] there are only a few reports on the Friedel-Crafts acylation of aromatic compounds with **1**.[3-4] The $AlCl_3$-catalyzed reaction of benzene with **1** was carried out under various conditions. Analysis for products was carried out after converting to the corresponding methyl esters. The results are summarized in **Scheme 1** and **Table 1**.

As shown in the Table, the $AlCl_3$-catalyzed acylation of benzene with **1** afforded a mixture of 2-benzoylphenylacetic acid (**2**), 2-phenacylbenzoic acid (**3**) and isobenzalphthalide (**4**) in any cases. It should be noted that formation of **2**, which was not yet reported in the previous paper,[3] was observed in the present work. Compound (**4**) might be formed from **3** in the presence of $AlCl_3$ catalyst. A excess of $AlCl_3$ catalyst and benzene was necessary to obtain the products in considerable yields. It was also found that the excess catalyst was specially favorable for the formation of **4**. Although detailed reaction mechanism of the acylation is still obscure, the following pathway as shown in **Scheme 2** can be proposed.

It is estimated from the above data of Table that K_1/K_2 values are 1.2～3.6. That is, the benzoylation and phenylacetylation occurred competitively, giving **2** and **3** including **4**. This suggests that the latter acylation should be more predominant that of the former acylation in this reaction. The same phenomenon was observed in the competitive acylation of benzene with a mixture of anhydrides of phenyl acetic acid and benzoyl acid.[5] However, the reaction rate for acylation of benzene with phenylacetic anhydride was about 70 times larger than that for the acylation of benzene with benzoic anhydride.[6-7]

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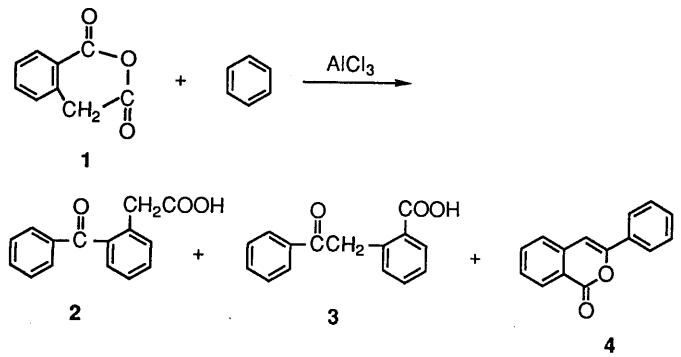
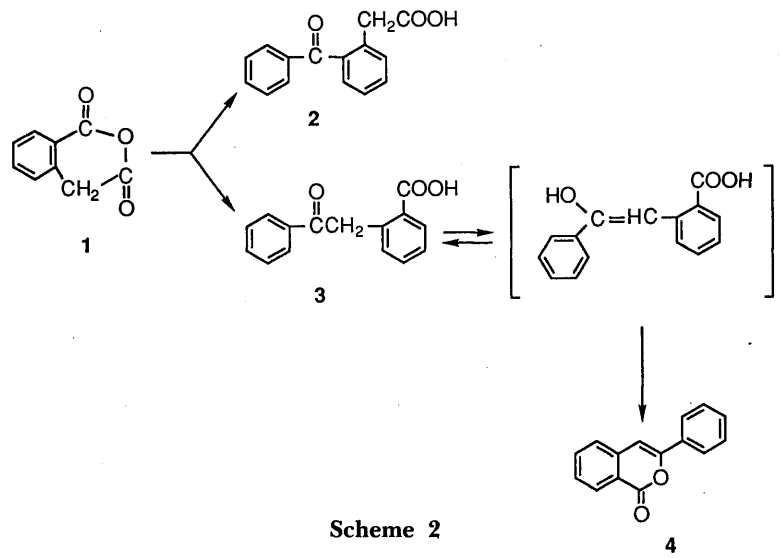
Table 1 $AlCl_3$-Catalyzed Acylation of Benzene with Homophthalic Anhydride (1)[a]

Run	$AlCl_3$/**1**	Benzene/**1**	Total yield (%)	Products (%)		
				2	**3**	**4**
1	1	25	15	6	9	trace
2	2	25	27	8	4	15
3[b]	2	25	17	4	13	trace
4[c]	2	25	23	5	18	trace
5[d]	2	25	48	17	22	9
6	4	25	55	15	9	31
7	6	25	58	17	9	32
8	4	50	61	18	33	10
9	4	75	54	12	32	10
10[e]	2	1	11	5	6	1
11[e]	2	1	11	4	2	5

a) 50℃, 5hr. b) Reaction temperature: 25℃. c) Reaction time: 0.5hr.
d) Reaction temperature: 60℃. e) 1.2-Dichloromethane (10ml) was used as a solvent.



Scheme 1



Scheme 2

Experimental Section

Typical Procedure. To a mixture of 20mmol of $AlCl_3$ in 25ml of benzene was added phthalic anhydride (5mmol) at 50℃ over a period of 5min. After the reaction mixture was stirred for more 5hr at the same temperature, it was poured into a large excess of ice-water and then organic layer was extracted with ethyl ether. The ether extract was washed several times with saturated sodium chloride solution, dried over sodium sulfate and evaporated in vacuo to give the residue which was esterified with an ether solution of diazomethane. The produced methyl esters were analyzed by means of HLPC employing a Shimazu LC-6A model on a 0.15m×6mm column packed with ODS. The acid (**2**) was isolated from the reaction mixture by preparative column chromatography (Shim-pack PREP-ODS, 0.25m×20mm column) and led to the methyl ether.

2: Methyl ester; colorless oil, IR (neat) 1660 and 1739 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.55 (3H, s), 3.90 (2H, s), 7.2-7.9 (9H, m); MS m/z 254 (M^+), 223 (M^+-OCH_3), 195 ($M^+-CO_2CH_3$), 177 ($M^+-C_6H_5$), 165 ($M^+-C_7H_5$), 149 ($M^+-COC_6H_5$), 105 ($COC_6H_5^+$).

3: colorless prisms, mp 160-161℃, methyl ester: mp 107-108.5℃; IR (KBr) 1686 and 1717 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.76 (3H, s), 4.74 (2H, s), 7.3-8.2 (9H, m); MS m/z 254 (M^+), 223 (M^+-OCH_3), 195 ($M^+-CO_2CH_3$), 165 ($M^+-COC_6H_5$), 105 ($COC_6H_5^+$).

4: colorless prisms, mp 85-86℃, IR (KBr) 1686 and 1726 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.79 (1H, broad s), 7.3-8.2 (9H, m); MS m/z 222 (M^+-CO), 165 ($M^+-C_7H_5$).

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