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Friedel-Crafts Reaction of Benzene with 2-Phenylpentanedioic Anhydride

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Synopsis. The reaction of benzene with 2-phenylpentanedioic anhydride in the presence of $AlCl_3$ afforded a mixture of 1,2,3,4-tetrahydro-4-oxo-1-naphthalenecarboxylic acid, 4-benzoyl-2-phenylbutanoic acid and the isomeric 4-benzoyl-4-phenylbutanoic acid. The relative yields among the products were markedly affected by a change in the polarity of the solvent.

In a previous paper[1] the $AlCl_3$-catalyzed acylation of benzene with 2-phenylbutanedioic anhydride (**1**) was reported. Competitive inter- and intramolecular acylations were reported in the above reaction system. It was also reported that either the oxonium compound or the acylium ion, which were derived from the interaction between **1** and $AlCl_3$, were the actual acylating agents. Therefore, in order to obtain more information on the actual acylating agent in the Friedel-Crafts reaction with the dibasic acid anhydride, it was necessary to investigate the Friedel-Crafts reaction with a higher dibasic acid anhydride.

Only a few works between benzene and 2-phenylpentanedioic anhydride (**2**) have so far been described[2,3] that **2** acylated intermolecularly benzene to give only 2-phenyl substituted keto acid under Friedel-Crafts conditions, although intramolecular reaction took place with sulfuric acid as catalyst.

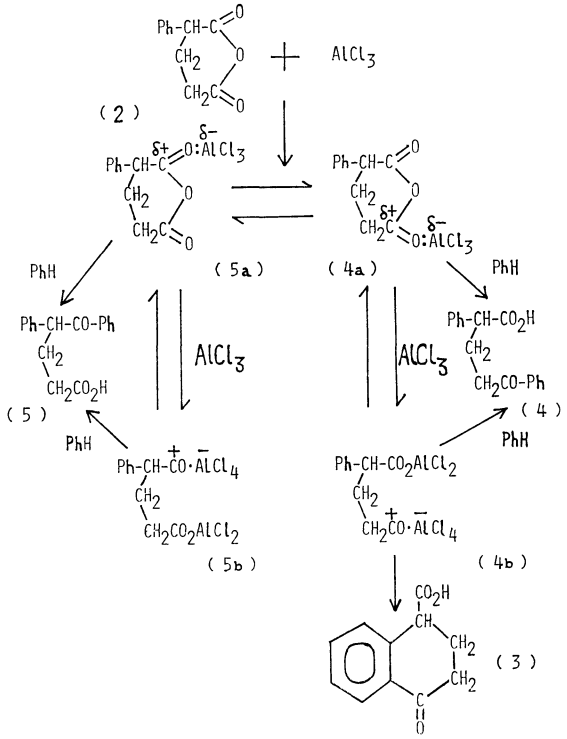
In the present study the Friedel-Crafts reaction of benzene with **2** was conducted in various solvents having different polarities, and the solvent effect examined in connection with the reaction mechanism.

The reaction of **2** with $AlCl_3$ in a large excess of benzene gave a mixture of 1,2,3,4-tetrahydro-4-oxo-1-naphthalenecarboxylic acid (**3**), 4-benzoyl-2-phenylbutanoic acid (**4**) and the isomeric 4-benzoyl-4-phenylbutanoic acid (**5**), as is shown in Table 1. However, the total yield of these keto acids was lower than that obtained from the acylation of benzene with **1** under similar reaction conditions, and the yield of **3** was always over the sum of those of **4** and **5**. This suggested that the intramolecular acylation of **2** with $AlCl_3$, even in a large excess of benzene, predominates over the intermolecular reaction of **2** on benzene in the presence of $AlCl_3$. A decrease in the amount of $AlCl_3$ from 20 to 10 mmol did not largely affect the distribution of products.

In more polar solvents such as 1,2-dichloroethane, the reaction of **2** with a limited amount of benzene predominantly gave **3** using 20 mmol of $AlCl_3$, accompanied by a small amount of **5** and a trace of **4**. Furthermore, in the case of 10 mmol of $AlCl_3$ on the reaction in 1,2-dichloroethane, **3** was exclusively obtained with a trace amount of **5**.

In nitrobenzene, the most polar solvent used, the reaction of **2** with benzene, in the presence of 30 mmol of $AlCl_3$, gave **3** almost exclusively. The intramolecular acylation of **2** with $AlCl_3$ in nitrobenzene overwhelmingly predominated over the intermolecular acylation of **2** on benzene in the presence of $AlCl_3$. The use of 30 mmol of $AlCl_3$ without benzene increased the yield of **3** to 79%.

These results imply that the solvent variations in the reaction of **2** with benzene in the presence of $AlCl_3$ markedly affect the relative yield among, **3**, **4**, and **5**; thus, an increase of polarity of solvent led to an increasing yield of **3** and the decreasing yields of **4** and **5**. From this, the following reaction paths may be formulated in consideration of the results obtained in the acylation of benzene with **1**.[1]



Scheme 1.

As delineated in Scheme 1, the oxonium compounds (**4a** and **5a**) possibly intermolecularly acylate benzene to give **4** and **5**, and also the acylium ions (**4b** and **5b**) afford **3**, **4**, and **5** by the intra- and intermolecular acylations. Since the above reaction gives **3** as the main product, which is obtained by way of **4b** and since the yield of **3** increases with increasing polarity of solvent, it may be assumed that the actual acylating agent in the reaction using **2** is a type of acylium ion. This is because the acylium ion bearing a more centered positive charge than the oxonium compound appears to be markedly influenced by a change of the polarity of solvent; hence, **4b** and **5b** reacted intermolecularly

Table 1. Acylation of benzene with 2-phenylpentanedioic anhydride at 30 °C

Solvent	Reaction time (h)	$AlCl_3$ (mmol)	C_6H_6 (mmol)	Product yields (%)[a]		
				3	**4**	**5**
None[b]	2	20	550	38	11	26
	2	10	550	23	5	13
$(ClCH_2)_2$ 25 ml	5	5	10	11	0	trace
	5	10	10	44	0	trace
	5	20	10	50	trace	8
	24	20	10	51	trace	7
	5	20	20	51	trace	14
	5	20	—	66	—	—
$C_6H_5NO_2$ 25 ml	24	20	10	66	0	trace
	24	30	10	70	0	trace
	24	30	20	65	trace	1
	24	30	—	79	—	—
None[b]	2	concd H_2SO_4 100	550	6	0	0
None[b]	2	CF_3SO_3H 5	550	23	0	0

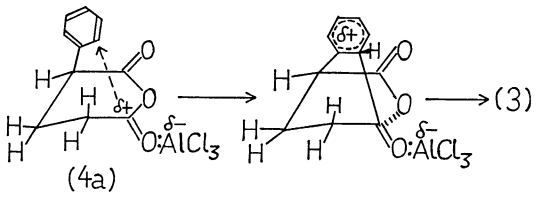
a) Calculated on the basis of the amount of 2-phenylpentanedioic anhydride used (10 mmol). b) The reaction was carried out at 60 °C, excess benzene being used as solvent.

with benzene to give **4** and **5**, respectively, although **4b** afforded **3** intramolecularly.

In nonpolar solvents such as benzene, the intermolecular acylations with **4b** and **5b** on the benzene molecule are possibly due to the low solvation of benzene, although the intramolecular acylation of **4b** predominates over the intermolecular acylations of **4b** and **5b** on benzene even in a large excess of benzene. In the intermolecular acylations, **5b** having an electron-attracting phenyl group closer to the acylium cation is preferred to **4b**. Hence the formation of **5** is more favored than **4**.

The highly charged acylium ions (**4b** and **5b**) may be strongly solvated by nitrobenzene to form a bulky acylating agent, and consequently the attack by such bulky agents upon benzene becomes intermolecularly difficult. Indeed, only the intramolecular acylation of **4b** occurred in nitrobenzene to give **3**, since the effect of solvent on the closely-located internal acylium ion and benzene ring is small.

If the phenyl group occupies a quasi axial position in **4a**, the formation of **3** should proceed with a direct intramolecular cyclization as follows:



Scheme 2.

However, the observed solvent effect can not be explained, because the effect of solvent upon the oxonium compound (**4a**) should be much less marked than for the acylium ion (**4b**). Moreover, the strained transition state, being caused by the intramolecular approach of $\overset{\delta+}{>}C{=}O{:}\overset{\delta-}{A}lCl_3$ to the benzene ring in **4a**, would have so high an energy that it would be improbable.

Since it is known[4] that trifluoromethanesulfonic acid is a very effective catalyst for the acylation of arenes, the reaction of **2** with a large excess of benzene in the presence of trifluoromethanesulfonic acid or concd sulfuric acid was attempted. However, only the intramolecular acylation of **2** occurred and the yield of **3** was considerably lower compared with the case using $AlCl_3$.

Experimental

Material. Compound **2** was prepared according to the method of Horning *et al.*

Acylation of Benzene with 2 in the Presence of $AlCl_3$. The procedure paralleled the acylation with **1** described in an earlier paper.[1]

Analyses of the Products. All keto acids were esterified with an ethereal solution of diazomethane and then analyzed by GLPC employing a Yanagimoto G-800T model on a 1.5 m × 3 mm column packed with Apieson Grease M (5 wt %) on Celite 545 of 80—100 mesh with a He flow of 40 ml/min at 228 °C. All methyl esters were identified by comparison of their retention times with those of authentic samples. The retention times of the methyl esters of **2**,[2] **3**,[2] **4**,[2,5] and **5**[5,6] were 1.0, 1.4, 4.2, and 5.6 min, respectively. 4-Chlorobenzophenone was used as the internal standard for the GLPC determination.

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