

Friedel-Crafts Reaction of Benzene with 2-Phenylbutanedioic Anhydride

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Synopsis. The AlCl_3 -catalyzed acylation of benzene with 2-phenylbutanedioic anhydride was found to give a mixture of 3-benzoyl-2-phenylpropanoic acid, isomeric 3-benzoyl-3-phenylpropanoic acid, and 3-oxoindan-1-carboxylic acid. The distribution of the products was affected markedly by the amount of AlCl_3 or solvents used.

It has been reported in earlier publications¹⁻⁵ that the acylation of benzene with 2-phenylbutanedioic anhydride (**1**) gave only the intermolecular acylation products, 3-benzoyl-2-phenylpropanoic acid (**2**) and 3-benzoyl-3-phenylpropanoic acid (**3**), in low yields (6.9 and 7.5%, respectively). However, the reaction mechanism discussed on the basis of such low yields does not appear to afford a rational mechanism, and furthermore, there is the possibility of intramolecular acylation of **1** itself. In the present work, the acylation of benzene with **1** was studied in more detail and the solvent effect was examined.

Results and Discussion

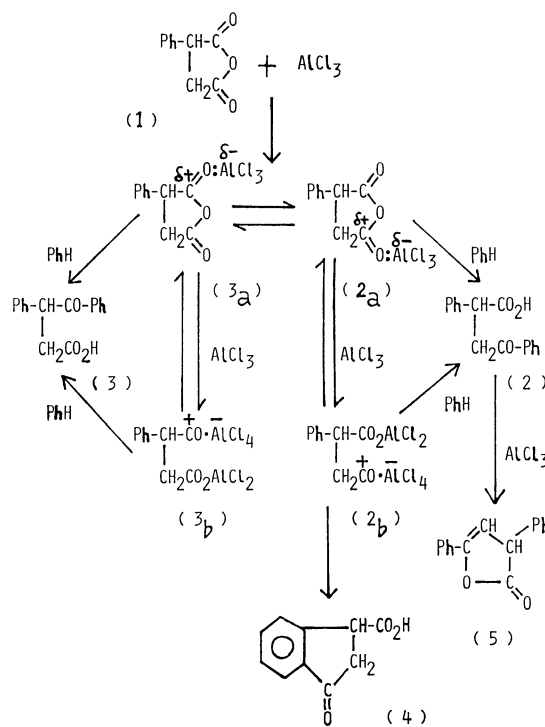
Ten mmol of **1** reacted almost quantitatively with 20 mmol of AlCl_3 in a large excess of benzene (550 mmol) to give a mixture of **2** and **3**, in which the yield of **3** was about twice as much as that of **2**.

When acylation using a lesser amount of benzene (10 mmol) was carried out in the presence of 20 mmol of AlCl_3 in 1,2-dichloroethane, a considerable amount of **4**, an intramolecular acylation product, was formed along with **2** and **3**. A high yield (93%) of **4** was also obtained in the absence of benzene using 1,2-dichloroethane as a solvent. These facts indicate that both inter- and intramolecular acylations occur competitively in the reaction system. A decrease in the amount of AlCl_3 in 1,2-dichloroethane resulted in a greater decrease in the yield of **3** than those of **2** and **4**, or higher $(2+4)/(3)$ ratio.

Acylation in nitrobenzene gave the same products, accompanied by a small amount of 2,4-diphenyl-3-buten-4-olide (**5**). However, the yield of **3** was low even with a greater amount (30 mmol) of AlCl_3 and it was always less than that of **2**.

These results suggest the following reaction paths: In the presence of a sufficient amount (20 mmol) of AlCl_3 , the acylating agent should be the acyl halide complexes (**2b** and **3b**), because one molecule of dibasic acid anhydride requires two molecules of AlCl_3 to form an acyl halide complex.⁶ The electrophilic reactivity of **3b** having an electron-attracting phenyl group closer to the acylium cation may be greater than that of **2b**, hence, **3** is formed preferentially, even though the concentration of **3b** is lower than that of species **2b** (or **2a**).

However, for an insufficient amount of AlCl_3 (10 mmol), complexes of the entire anhydride molecule



Scheme 1.

coordinated with one molecule of AlCl_3 (**2a** and **3a**) should appear as the actual acylating agents.⁷ The concentration of the complex, **2a**, in which AlCl_3 is added to the oxygen atom separated from the phenyl group, should be higher than that of **3a** (or **3b**). Complex **2a** should afford **2** and **4** upon acylation, although **4** may be formed preferentially via **2b**. Therefore, a decrease in the amount of AlCl_3 leads to an increase in the ratio $(2+4)/(3)$.

Since nitrobenzene is a polar solvent, the polarized complexes (**2b** and **3b**) should be strongly solvated by nitrobenzene to form bulky acylating species. Such bulky acylating species may be unfavorable for the electrophilic attack on the benzene molecule, hence, the yields of **2** and **3** become low. Furthermore, the complex formation between nitrobenzene and AlCl_3 may decrease the effective amount of AlCl_3 and thus unfavorably affect the formation of **3a** (or **3b**) with the result that the yield of **3** is low.

The reaction of isolated **2** with AlCl_3 in nitrobenzene gave **5** via the enolization of **2**.

Experimental

General Procedure for the Acylation of Benzene with 2-Phenylbutanedioic Anhydride (1). To a solution of benzene and AlCl_3 in $\text{ClCH}_2\text{CH}_2\text{Cl}$ was gradually added a solution of **1** in $\text{ClCH}_2\text{CH}_2\text{Cl}$. The reaction mixture was stirred at 25°C for 5 h, poured onto crushed ice containing 6 ml of concd

TABLE 1. AlCl_3 -CATALYZED ACYLATION OF BENZENE WITH 2-PHENYLBUTANEDIOIC ANHYDRIDE (10 mmol) AT 25 °C FOR 5 h

Solvent	AlCl_3 (mmol)	C_6H_6 (mmol)	Product yields ^{a)} (%)			(2+4) (3)
			2	3	4	
None	10	550	19	29	trace	0.7
	20	550	29	69	trace	0.4
	30	550	30	69	trace	0.4
$(\text{ClCH}_2)_2$ 10 ml	20	0	—	—	93	
	30	0	—	—	93	
	5	10	3	7	6	1.3
	10	10	7	18	12	1.1
	20	10	21	59	19	0.7
	10	20	11	28	9	0.7
	20	20	24	66	9	0.5
	30	0	—	—	39	
	20	10	10	5	16	5.2
$\text{C}_6\text{H}_5\text{NO}_2^{\text{b)}$ 10 ml	30	10	14	10	23	3.7 ^{c)}
	30	20	25	15	23	3.3 ^{c)}

a) Calculated on the basis of the amount of 2-phenylbutanedioic anhydride used. b) The reaction time was one day. c) **5** was obtained in a yield of less than 1%.

HCl, and then extracted with ether. After removal of the solvent, the crude keto carboxylic acids were methylated with an ethereal solution of diazomethane. The resulting esters were analyzed by means of GLPC employing a Yanagimoto G 800 T Model chromatograph on a 1.5 m × 3 mm column packed with Apiezon Grease M (5 wt%) with a He flow of 40 ml/min at 205 °C. Benzyl benzoate was used as an internal standard.

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