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# 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-pehnylpropanoic 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 publications[1–5] 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

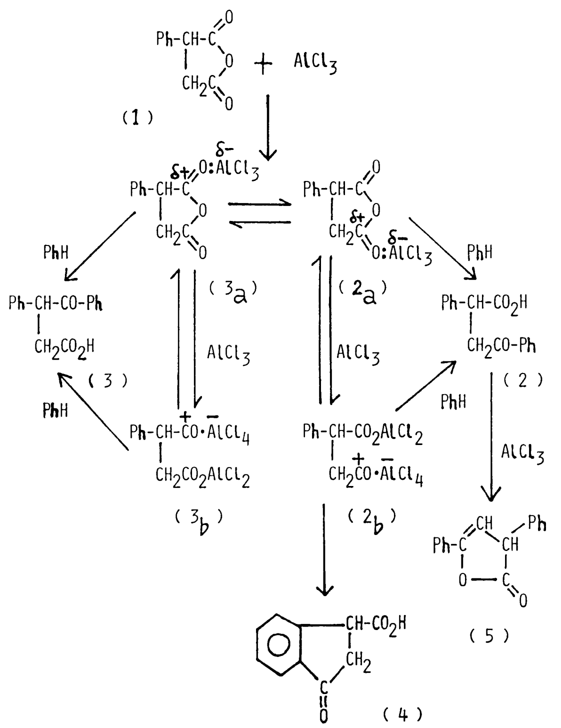
Ten mmol of **1** reacted almost quantitatively with 20 mmol of $AlCl_3$ in a large excess of benzene (550 mmol) to give a mixture of **2** and **3**, in which the yield of **3** was about twice as much as that of **2**.

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 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**).



Scheme 1.

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 $ClCH_2CH_2Cl$ was gradually added a solution of **1** in $ClCH_2CH_2Cl$. 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) (%) | | | $\frac{(\mathbf{2}+\mathbf{4})}{(\mathbf{3})}$ |
|---|---|---|---|---|---|---|
| | | | **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 |
| $(ClCH_2)_2$ | 20 | 0 | — | — | 93 | |
| 10 ml | 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 |
| $C_6H_5NO_2$ b) | 30 | 0 | — | — | 39 | |
| 10 ml | 20 | 10 | 10 | 5 | 16 | 5.2 |
| | 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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