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https://doi.org/10.15017/17247

出版情報：九州大学大学院総合理工学報告. 13 (4), pp.361-365, 1992-03-01. 九州大学大学院総合理工学研究科
バージョン：
権利関係：

九州大学大学院総合理工学研究科報告
第13巻 第4号 361-365頁 平成4年3月

Engineering Sciences Reports, Kyushu University
(KYUSHU DAIGAKU SOGORIKOGAKU KENKYUKA HOKOKU)
Vol. 13, No. 4, pp. 361 - 365, MAR. 1992

$AlCl_3$-Catalyzed Competitive Reaction of Benzene and Monosubstituted Benzenes with Phthalic Anhydride: Intra- and Intermolecular Selectivities

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(Received November 30, 1991)

The $AlCl_3$-catalyzed acylation of benzene and monosubstituted benzenes with phthalic anhydride was carried out under various conditions in order to obtain an information about the substrate selectivity (as expressed by K_{Ar}/K_B) and positional selectivity (estimated by isomer distribution). It was also found that substrate selectivity of anisole against benzene was very high.

Friedel-Crafts acylation of aromatic compounds with phthalic anhydride (**1**) has been widely used in a field of organic synthesis.[1] Although there are some reports on the substrate (intermolecular) and positional (intramolecular) selectivities in the Friedel-Crafts acylation of aromatic compounds,[2-3] these selectivities in the acylation with **1** is still unknown by now.

We now wish to report Friedel-Crafts competitive acylation of benzene and monosubstituted benzenes such as alkyl-and halobenzene derivatives with **1** under the various conditions.

Since the competitive method of rate determination can be employed only when the observed relative rates are indeed first order dependent upon the concentrations of the competing aromatic substrates, and product distributions are obtained under kinetically controlled conditions (free of isomerizations, i. e., independent on the reaction time). An influence of a variation for the concentration of benzene and toluene on the substrate selectivity (K_T/K_B value) and positional selectivities were investigated (**Scheme 1**). The conversion from **1** to **2** and **3a** was very good in any case (generally 80 ~ 95%). The results of **Table 1** confirm the competitive acylation has apparently first order dependence on the concentrations of aromatic substrates. The substrate and positional selectivities were determined by GC analysis of methyl esters (**4**) of **2** and **3a** produced by treatment with diazomethane in ether solution since the ketoacids **2** and **3a** could not be detected by GC.

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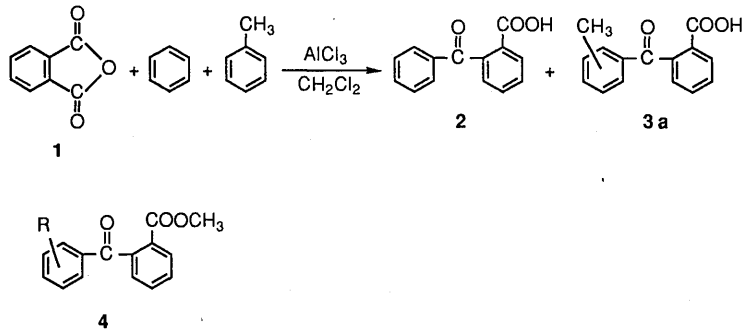


Scheme 1

Table 1 $AlCl_3$-Catalyzed Competitive Reaction of Benzene and Toluene with Phthalic Anhydride (**1**)[a]

Run	Toluene/Benzene (mol/mol)	K_T/K_B	Isomer distribution of **3a** (%) Ortho	Meta	Para
1	1/1	191	2.2	1.5	96.3
2	1/3	188	2.1	1.4	96.3
3	1/6	213	2.2	1.6	96.2
4	1/10	210	2.2	1.6	96.2
	Average	201	2.2	1.5	96.3

a) 15℃, 10min.

The effect of the reaction time on the substrate and positional selectivities was also investigated (**Scheme 1**, **Table 2**). The data indicate that an elongation of the reaction time show no significant difference on the isomer distributions. It is, therefore, clear that

Table 2 Intra-and Intermolecular Selectivities on Friedel-Crafts Acylation of Benzene and Toluene with Phthalic Anhydride (**1**)[a]

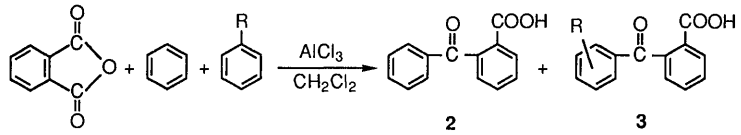
Run	Time (min.)	Conversion (%)	K_T/K_B	Isomer distribution of **3a** (%) Ortho	Meta	Para
1[b]	5	89	206	2.1	1.5	96.4
2[b]	10	90	191	2.2	1.5	96.3
3[c]	10	96	188	2.2	1.5	96.3
4[b]	15	89	196	2.1	1.3	96.6
5[b]	20	97	195	2.2	1.5	96.3
6[d]	10	87	166	2.2	1.6	96.2
7[e]	10	93	181	2.1	1.4	96.5

a) $AlCl_3$/anhydride: 2/2. b) Benzene/toluene/anhydride: 5/5/1.
c) Benzene/toluene/anhydride: 10/10/1. d) Benzene/toluene/anhydride: 4/16/1.
e) $AlCl_3$/anhydride: 3/1. Benzene/toluene/anhydride: 4/16/1.

non-isomerizing conditions for the present acylation are experimentally proved.

In order to clarify a correlation between a basicity of aromatic substrate and both the substrate and positional selectivities in the acylation with **1**, competitive acylations of benzene and various monosubstituted benzenes were undertaken in the presence of two equivalents of $AlCl_3$ in 1, 2-dichloromethane (**Table 3**). The produced ketobenzoic acids [**3a**(R $=CH_3$), **3b**(R $=CH_2CH_3$), **3c**(R $=CH(CH_3)_2$), **3d**(R $=C(CH_3)_3$), **3e**(R $=OCH_3$), **3f**(R $=F$), **3g**(R $=Cl$), **3h**(R $=Br$)] were converted to the corresponding methyl esters (**4a-4h**) with the same way as described above to analyze them by GC.

Table 3 $AlCl_3$-Catalyzed Competitive Acylation of Benzene and Monosubstituted Benzene with Phthalic Anhydride (1)[a)]

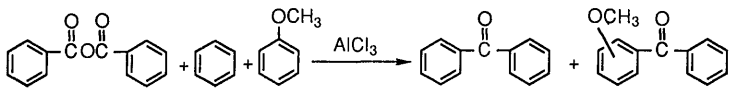


1　　2　　3

Aromatic compound	K_T/K_B	Isomer distribution of **3** (%) Ortho	Meta	Para
Toluene	191	2.2	1.5	96.3
Ethylbenzene	199	1.7	1.6	96.7
Isopropylbenzene	195	0.6	1.5	97.9
t-Butylbenzene	122	0.8	2.3	96.9
Anisole	700	1.4	1.7	97.6
Fluorobenzene	0.1	0	0	100
Chlorobenzene	0.07	0	0	100
Bromobenzene	0.03	0	0	100

a) 40℃, 10min.

Brown et al.,[4] reported that the relative rate constants (K_{Ar}/K_B values) in the $AlCl_3$-catalyzed acetylation of alkylbenzenes with acetyl chloride were almost same values. While Olah et al.,[5] pointed out that the values of K_{Ar}/K_B gradually decreased with increasing of branch of the alkyl group in the $AlCl_3$-catalyzed acylation with acetyl chloride in nitromethane at 25℃. Although it was previously reported[3] that the increasing of branch of alky group from methyl group to tert-butyl group decreased gradually the corresponding K_{Ar}/K_B values in the acylations with acetic and benzoic anhydride. However, such phenomenon was not observed in the present work. It should be noted that the substrate



5　　6　　7

Scheme 2

selectivity in the competitive acylation of benzene and anisole with **1** is a very large value of 700, on the contrary the isomer distribution is almost the same as that of alkylbenzenes. It was also found that the substrate selectivity in the competitive benzoylation of benzene and anisole with benzoic anhydride (**5**) is low (Scheme 2), that is, $K_{Ar}/K_B=18$ (isomer distribution: ortho; 0.3, meta; 2.1 and para; 97.6%)

It is not clear why such a difference is observed. However, there is a possible elucidation that transition state in the determination step of the acylation with **1** resembles δ-complex but not π-complex. In the case of the reaction with benzoyl anhydride, however, $AlCl_3$ may react with anisole to form a complex which should be less active than anisole itself.

The competitive acylation of benzene and halobenzenes showed that the substantially decreased reactivities in the order of fluoro-, chloro-, and bromobenzene. This is the order anticipated on the basis of conjugate property of the three halogen atoms and in accord with the results from the other electrophilic substitution against these halobenzenes.

Experimental Section

Typical Procedure. To a mixture of 10mmol of $AlCl_3$ in 5ml of 1, 2-dichloromethane was added at 15℃ over a period of 5min a solution of 25ml of toluene and 5mmol of phthalic

Table 4 The Retention Times of Methyl Ketobenzoates (**4**)[a)]

4	R	Retention Time (min)
4i	H	9.5
4a	o-CH_3	10.6
	m-CH_3	11.8
	p-CH_3	13.6
4b	o-CH_2CH_3	6.0
	m-CH_2CH_3	6.6
	p-CH_2CH_3	7.8
4c	o-$CH(CH_3)_2$	6.1
	m-$CH(CH_3)_2$	7.0
	p-$CH(CH_3)_2$	8.6
4d	o-$C(CH_3)_3$	6.1
	m-$C(CH_3)_3$	7.6
	p-$C(CH_3)_3$	9.8
4e	o-OCH_3	6.1
	m-OCH_3	7.4
	p-OCH_3	9.9
4f	p-F	8.6
4g	p-Cl	11.0
4h	p-Br	13.5

a) Capillary column: Silicon OV-1701, 25m×0.25mϕ. Carrier gas: nitrogen 1.5ml/min. Column Temperature: 240℃ except **4i**, **4a**, and **4f** (210℃).

anhydride in 5ml of 1,2-dichloromethane. After the reaction mixture was stirred for more 10min 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 GC. The yields of products obtained in the present work were very good, 80～90%. The retention times of methyl ketobenzoates obtained in this work were summarized in **Table 4.**

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