tert-Butylation of Aromatic Hydrocarbons with AlCl₃-tert-Butylanisole Catalyst*

by Keizo Shimada**

Summary: *tert*-Butylation of aromatic hydrocarbons with *tert*-butyl chloride in the presence of AlCl₃-*tert*-butylanisole was investigated. Neither isomerization of the products nor transalkylation of the substrate with the products was observed when the molar ratio of *tert*-butylanisole to AlCl₃ was more than two. Competitive *tert*-butylation of benzene and toluene showed higher substrate selectivity ($k_A/k_B=21-24$). A role of trans-*tert*-butylation in the *tert*-butylation was suggested from the results of *tert*-butylation of toluene in the presence of 2,4- and 2,5-dimethylanisole.

1 Introduction

It is well known that a *tert*-butyl group cannot be introduced into an *ortho* position of an alkyl group in the aromatic substitution reaction owing to the steric hindrance of the bulky *tert*-butyl group, and this fact is applied to the separation of isomeric alkylbenzenes and alkylphenols¹⁾.

The author²⁾ has reported that aromatic hydrocarbons can be trans-*tert*-butylated by 2,4-di-*tert*-butylanisole in the presence of AlCl₃ without secondary reactions such as the isomerization of *tert*-butylated products and transalkylation of the aromatic hydrocarbons.

This paper deals with the *tert*-butylation of aromatic hydrocarbons with *tert*-butylchloride in the presence of the AlCl₃-*p*-*tert*-butylanisole catalyst. This *tert*-butylation with the present catalyst system, which is similar to the trans-*tert*-butylation with 2,4-di-*tert*-butylanisole described above²⁾, possesses higher substrate selectivity than any of the previously known *tert*-butylation³⁾, and it may be useful for the separation of isomeric aromatic hydrocarbons by the kinetically controlled *tert*-butylation.

2 Experimental

2.1 Materials

2.1.1 Hydrocarbons

Benzene, toluene, ethyl- and isopropylbenzene of guaranteed reagent grade were purified by distillation, and their purity was analyzed to be 99.9% by gas chromatography. Guaranteed reagent *m*-xylene was *tert*-butylated with di-*tert*-butyl-

toluene⁴⁾ in the presence of AlCl₃, and the *tert*-butyl-*m*-xylene separated by distillation was de-butylated using toluene. The *m*-xylene fraction freed from *p*-xylene thus obtained was purified by distillation, and its purity was higher than 99.5%. *o*-Xylene was purified in the same way.

2.1.2 Anisoles

p-*tert*-Butylanisole was prepared by the method described previously²⁾. 2,4- and 2,5-Dimethylanisoles were obtained by methylation of the corresponding xylenols with dimethyl sulfate. (b.p. 190°C (lit.⁵⁾ 192°C) and 188°C (lit.⁶⁾ 186~8 °C), respectively.)

2.2 Reactions

To a mixture of benzene (or alkylbenzene) and *tert*-butylanisole (or other anisole derivatives) an appropriate amount of AlCl₃ was dissolved, and *tert*-butyl chloride was added all at once with stirring. (Reaction temperature is shown in **Table 1~7**) Samples were taken at appropriate intervals, poured into ice water, and washed and dried over calcium chloride. The samples were analyzed by a gas chromatograph using Apiezone L (10%) on Diasolid S column (2 m) at 180°C or Carbowax 4000 (10%) on Diasolid A column (2 m) at 170°C (for isopropylbutylbenzenes).

3 Results and Discussion

The results of the *tert*-butylation of toluene with *tert*-butyl chloride in the presence of AlCl₃-*tert*-butylanisole are shown in **Table 1**.

tert-Butylation of toluene with *tert*-butyl halide in the presence of aluminum halide is usually accompanied with rapid isomerization. For example, Brown's⁷⁾ experiment which was carried out using a special flow reactor under a contact

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Table 1 *tert*-Butylation of Toluene with AlCl_3 -*tert*-Butylanisole Catalyst at 25°C
Reactant : Toluene 0.5 mol; *t*-BuCl 0.5 mol

Catalyst (mol)		Time	Anisol Deriv. mol%			Toluene Deriv. mol%		<i>t</i> -Bu-Toluene <i>p</i> -(%)
AlCl_3	<i>t</i> -Bu-A		A	<i>p</i> - <i>t</i> -Bu-A	di- <i>t</i> -Bu-A	<i>t</i> -Bu-	di- <i>t</i> -Bu-	
0.05	0.5	2 min	0.5	70.0	29.5	1.6	0	
		5 "	0.7	69.2	30.1	2.5	"	
		10 "	0.7	69.5	29.8	4.5	"	
		20 "	0.5	70.6	28.8	8.5	"	94.6
		1 hr	0.8	73.1	26.1	20.6	"	93.8
		3 "	1.2	80.8	18.0	43.7	"	94.2
		20 "	3.4	88.6	8.0	79.0	"	94.5
		45 "	4.9	90.3	4.8	89.4	"	94.8
0.05	0.1	2 min	0	79.3	20.7	38.2	0	93.5
		5 "	"	82.5	17.5	57.2	"	94.3
		10 "	"	87.0	13.0	65.7	"	94.0
		20 "	1.7	90.0	7.5	76.4	"	94.5
		1 hr	0	97.5	2.5	89.2	"	94.3
		2 "	"	98.5	1.5	92.7	"	94.4
		18 "	3.0	97.0	0	98.0	2.0	93.5
		23 "	3.3	95.7	1.0	97.8	2.2	93.8
0.02	0.02	3 min	0	100	0	79.3	0.7	93.5
		5 "	"	"	"	83.8	0.8	93.8
		10 "	"	"	"	86.9	1.0	94.2
		20 "	"	"	"	92.0	1.2	94.2
		1 hr	"	"	"	91.0	2.4	94.2
		2 "	"	"	"	89.5	3.8	93.8
		4 "	"	"	"	89.5	5.8	92.4
		7 "	"	"	"	89.2	8.0	90.7

A : Anisole

time of 0.005 sec. resulted in an isomer distribution of *p* : *m* = 30.5 : 69.5. Later, Olah et al.³⁾ showed that this isomerization was observed in nitromethane solution. They⁸⁾ also reported the isomerization of *p*-*tert*-butyltoluene with AlCl_3 in nitromethane solution at room temperature.

In this work, when toluene was *tert*-butylated using an equimolar ratio of AlCl_3 and anisole, *tert*-butyltoluene produced suffered isomerization, and 2,4-di-*tert*-butylanisole was not detected in the reaction mixture. However, when the amount of AlCl_3 was reduced to less than a half mol of *tert*-butylanisole, di-*tert*-butylanisole was formed immediately after the addition of *tert*-butyl chloride and then decreased gradually. The concentration of *tert*-butyltoluene increased monotonously, and finally most of the *tert*-butyl group added was transferred to toluene. There was no sign of isomerization of *tert*-butyltoluene.

The results of the *tert*-butylation of benzene, ethylbenzene and isopropylbenzene are shown in Table 2~4. The mode of the reactions was the same as the *tert*-butylation of toluene. Thus it seems that toluene (or other alkybenzene) is trans-*tert*-butylated by 2,4-di-*tert*-butylanisole, which is produced by the preferential attack on *tert*-butyl chloride to *p*-*tert*-butylanisole. Another explanation is that the *tert*-butylation of *p*-*tert*-

Table 2 *tert*-Butylation of Benzene with AlCl_3 -*tert*-Butylanisole Catalyst at 25°C
Reactant : Benzene 0.5 mol; *t*-BuCl 0.5 mol
Catalyst : AlCl_3 0.05 mol; *t*-Bu-Anisole 0.5 mol

Time	Anisole Deriv. mol%			Benzene Deriv. mol%	
	A	<i>p</i> - <i>t</i> -Bu-A	di- <i>t</i> -Bu-A	<i>t</i> -Bu-	<i>p</i> -di- <i>t</i> -Bu-
2 min	0	68.4	31.6	0.7	0
5 "	"	68.0	32.0	0.7	"
10 "	"	67.8	32.2	1	"
20 "	"	67.2	32.8	1	"
1 hr	"	66.6	33.4	2	"
2 "	"	67.9	32.1	2	0.7
19 "	1.2	76.8	22.0	4.0	16.3
70 "	1.8	85.3	12.8	4.5	34.8

A : Anisole

Table 3 *tert*-Butylation of Ethylbenzene with AlCl_3 -*tert*-Butylanisole Catalyst at 25°C
Reactant : EtPh 0.5 mol; *t*-BuCl 0.5 mol
Catalyst : AlCl_3 0.05 mol; *t*-Bu-Anisole 0.5 mol

Time	Anisol Deriv. mol%			Et-B. Deriv. mol%	
	A	<i>p</i> - <i>t</i> -Bu-A	di- <i>t</i> -Bu-A	Bu-Et-B	Bu-Et-B <i>p</i> -(%)
1 min	0	70.6	29.4	0.7	
5 "	"	69.4	30.6	2.2	
10 "	"	70.0	30.0	4.7	93.6
20 "	"	71.7	28.3	8.4	93.6
1 hr	"	75.2	24.8	22.5	93.3
2 "	"	79.2	20.8	35.2	93.6
4 "	"	83.5	16.5	51.3	93.5
17.5 "	2.6	89.3	8.1	81.4	94.0

A : Anisole, B : Benzene

Table 4 *tert*-Butylation of Isopropylbenzene with AlCl_3 -*tert*-Butylanisole Catalyst at 25°C
 Reactant : *i*-PrPh 0.5 mol; *t*-BuCl 0.5 mol
 Catalyst : AlCl_3 0.05 mol; *t*-Bu-Anisole 0.5 mol

Time	Anisole Deriv. mol%			<i>i</i> -Pr-B. Deriv. mol%	Bu- <i>i</i> -Pr-B <i>p</i> -(%)
	A	<i>p</i> - <i>t</i> -Bu-A	di- <i>t</i> -Bu-A	Bu- <i>i</i> -Pr-B	
2 min	0	69.9	30.1	1.5	
5 "	"	70.2	29.8	3.4	
10 "	"	70.7	29.3	6.1	93.5
20 "	"	71.8	28.2	12.2	93.5
1 hr	"	76.2	23.8	31.4	93.8
2 "	"	80.0	20.0	46.5	93.9
4 "	"	83.5	16.5	61.0	94.0
24 "	7.0	86.0	7.0	86.0	94.5

Table 5 *tert*-Butylation of Toluene with AlCl_3 -2,5- and 2,4-Dimethylanisole Catalyst at 20°C
 Reactant : Toluene 0.25 mol; *t*-BuCl 0.1 mol
 Catalyst : AlCl_3 0.01 mol; 2,5- or 2,4-Dimethylanisole 0.03 mol

Time	Conversion of Toluene to <i>t</i> -Bu-Toluene (%)		Ratio
	2,5-Me ₂ A	2,4-Me ₂ A	
0	0	0	(0.5)
1 min	4.2	8.2	0.51
2 "	7.2	11.3	0.64
5 "	15.8	22.0	0.72
10 "	24.1	32.4	0.74

butylanisole is a fast equilibrium reaction and the butylation of toluene is proceeded by the attack on the usual *tert*-butylation species, $t\text{-Bu}^+\cdot\text{AlCl}_4^-$ ·*p*-*t*-Bu-Anisole.

To clarify this point, *tert*-butylation reactions of toluene in the presence of 2,4- and 2,5-dimethylanisole were carried out. The results are shown in **Table 5**. The relative reaction rate of 1 : 0.5 at time zero was obtained by extrapolation. Considering the inductive effect of the methyl groups, 2,5-dimethylanisole may be a weaker base than 2,4-dimethylanisole.* Therefore, the complex of AlCl_3 with 2,5-dimethylanisole may be a stronger acid (catalyst) than that with 2,4-isomer. Now, if the *tert*-butylation proceeds exclusively by attacking the usual species, $t\text{-Bu}^+\cdot\text{AlCl}_4^-$ ·diMe-Anisole, a reverse result may be expected. Accordingly, the increase in the rate of *tert*-butylation in the presence of 2,4-dimethylanisole can be attributed to the concurrent trans-*tert*-butylation by 2,4-dimethyl-6-*tert*-butylanisole. On the other hand, 2,5-dimethylanisole could not be *tert*-butylated because of the steric hindrance by the methyl group of 5-position.

* Correlation of the basicity of aromatic ethers and σ^* induction constants was discussed by Agaeva et al. (*Azerb. Khim. Zh.*, 1972, (1), 69)

Table 6 Competitive *tert*-Butylation of Benzene and Toluene with AlCl_3 -*tert*-Butylanisole Catalyst at 17°C

Reactant : Benzene 0.25 mol; Toluene 0.25 mol;
t-BuCl 0.05 mol
 Catalyst : AlCl_3 0.025 and 0.01 mol;
t-Bu-Anisole 0.05 mol

AlCl_3 (mol)	Time	Conversion (%) of <i>t</i> -BuCl to		Substrate Selectivity k_T/k_B
		<i>t</i> -Bu-benzene	<i>t</i> -Bu-toluene	
0.025	4 min	1.0	21.0	21.0
	10 "	2.3	49.1	21.4
	30 "	4.3	86.8	20.2
0.01	30 min	0.5	11.8	24.9
	80 "	1.1	27.6	24.1

Table 7 Competitive *tert*-Butylation of Benzene and C₈ Aromatics with AlCl_3 -*tert*-Butylanisole Catalyst

Reactant : Aromatic 0.25 mol; Benzene 0.25 mol; *t*-BuCl 0.05 mol
 Catalyst : AlCl_3 0.01 mol, *t*-Bu-Anisole 0.05 mol

Aromatic	Temp. (°C)	Substrate Selectivity k_{Arom}/k_B
Ethylbenzene	17	21.6 ± 2.5
<i>m</i> -Xylene	20	2.14 ± 0.32
<i>o</i> -Xylene	"	139 ± 13

* Benzene 1.25 mol was used.

Thus, it seems likely that the trans-*tert*-butylation by 2,4-di-*tert*-butylanisole plays a role in the *tert*-butylation of aromatic hydrocarbons in the presence of *tert*-butylanisole- AlCl_3 catalyst.

Competitive *tert*-butylation of benzene and toluene, as well as that of the C₈ aromatics, was carried out. The results are shown in **Table 6** and **7**. The substrate selectivity k_T/k_B (21~24) was higher than that (14~16) obtained with SnCl_4 or AlCl_3 -nitromethane catalysts reported by Olah et al.^{3) *tert*-Butylation of C₈ aromatics also showed higher substrate selectivity (**Table 7**), which is important for the stepwise separation of hydrocarbons.}

An application of this new selective *tert*-butylation to the kinetically controlled stepwise separation C₈ aromatic hydrocarbons has been reported elsewhere^{9).}

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