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Transbutylation of Aromatic Hydrocarbons with Di-*t*-butylanisole[1)]

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The trans-*t*-butylation of aromatic hydrocarbons with di-*t*-butylanisole in the presence of aluminum chloride was studied. It was found that the *t*-butyl group substituted at the *ortho* position to the methoxy group transfered easily to the hydrocarbons, but the *t*-butyl group of the *para* position did not transfer to the hydrocarbons. The transbutylation products did not suffer further isomerization when the catalyst aluminum chloride was less than 1/2 mol of the di-*t*-butylanisole used. Competitive trans-*t*-butylation was carried out and k_T/k_B, k_{m-X}/k_B, k_{O-X}/k_B, and k_{EB}/k_B were found to be 24, 2.2, 136, and 19, respectively.

Trans-*t*-butylation of aromatic hydrocarbons with *t*-butylbenzenes has been reported mainly in connection with the separation of *p*-xylene from a xylene mixture*,[2)] on the basis that *p*-xylene could not be *t*-butylated because of the steric hindrance of the *ortho* position to the methyl group.[3)]

However, no report is available concerning the use of a *t*-butylation reagent having substituents other than alkyl groups on the aromatic ring.

In this paper, the trans-*t*-butylation of aromatic hydrocarbons with 2,4-di-*t*-butylanisole is described.

Experimental

Materials. *Hydrocarbons*: Guaranteed pure reagents of benzene, toluene, ethyl- and isopropylbenzene were purified through distillation. The resulting purities were higher than 99.9%, as confirmed by gas chromatographic analysis. Guaranteed pure reagents of *m*-xylene were *t*-butylated with di-*t*-butyltoluene[2)] in the presence of $AlCl_3$ and the butyl-*m*-xylene separated by distillation was debutylated using toluene. The xylene fraction free of *p*-xylene thus obtained was purified by distillation. The resulting purity was greater than 99.5%. *o*-Xylene was purified in the same way. *t*-Butylbenzene was synthesized from benzene and *t*-butyl chloride.

Anisole: A guaranteed pure reagent of anisole was distilled after washing with a 10% sodium hydroxide aqueous solution and water, with a resulting purity greater than 99.5% (analyzed by gas chromatography).

t-Butyl chloride was synthesized from guaranteed pure reagents of *t*-butyl alcohol and hydrochloric acid (38%), washed well with water and distilled twice.

p-t-*Butylanisole*: To a solution of $AlCl_3$ (90 g) in anisole (756 g), maintained at 10 °C, *t*-butyl chloride (650 g) was added for 3 h. Afterward, the reaction mixture was stirred for 6 h, ice–water was added to the mixture and the catalyst was decomposed. The organic layer was washed with water and an alkaline aqueous solution, dried and distilled. The fraction boiling at 218—222 °C was collected. Yield 560 g. Further purification through redistillation was carried out (bp 220—221 °C, purity greater than 99.5%).

*2,4-Di-*t*-butylanisole*: To a solution of $AlCl_3$ (50 g) in anisole (540 g), 1100 g of *t*-butyl chloride was added and stirred for 6 h at 10 °C. After decomposition of the catalyst by the addition of ice–water, the organic layer was washed with water and an alkaline aqueous solution and dried. 2,4-Di-*t*-butylanisole was crystallized by cooling. It was recrystallized three times from methanol (mp 36 °C (lit, 36—37 °C),[4)] yield 350 g). An additional 110 g of pure 2,4-di-*t*-butylanisole was obtained from a parent solution (393 g) through distillation and recrystallization from methanol.

Reactions. To a mixture of 0.1 mol each of benzene or alkylbenzenes and di-*t*-butylanisole, the desired amount of $AlCl_3$ was added with stirring. In the case of competitive reactions, a desired amount of $AlCl_3$ was added to a mixture of 0.5 mol of each of the aromatic hydrocarbons and 0.1 mol of di-*t*-butylanisole with stirring. The competitive reaction of benzene and *o*-xylene was carried out using 0.5 mol of benzene and 0.1 mol of *o*-xylene. Samples were taken at appropriate times, poured into ice–water, washed and dried over calcium chloride. The samples were analyzed by gas chromatography using Apiezone L (10%) on a Diasolid S column (2 m) at 180 °C.

Results and Discussion

Butylation of Toluene: The results are shown in Table 1 and 2.

Friedel-Crafts *t*-butylation of toluene has been investigated by many authors. Allen and Yats[5)] have

Table 1. Butylation of toluene with di-*t*-butylanisole at 20 °C $AlCl_3$ 0.02 mol

Time	mol % of anisole deriv.		mol % of toluene deriv.	
	p-*t*-Butylanisole	di-*t*-Butylanisole	*t*-Butyltoluene	*p*-Isomer content in *t*-butyltoluene
5 min	42.9	57.1	43.0	92.3
30 min	53.6	46.4	53.5	93.1
1 hr	57.5	42.5	57.5	92.8
3 hr	66.4	33.6	66.5	94.5
10 hr	73.2	26.8	73.2	94.5
24 hr	82.1	18.9	82.0	94.6
100 hr	91.4	8.5	91.3	94.6

Table 2. Butylation of toluene with di-*t*-butylanisole $AlCl_3$ 0.01 mol

Time	25 °C		50 °C	
	Conversion (%)	*p*-Isomer content in *t*-butyltoluene (%)	Conversion (%)	*p*-Isomer content in *t*-butyltoluene (%)
5 min	19.3	94.4	37.3	89.9
15 min	30.6	94.3	49.0	90.8
30 min	35.6	94.3	58.0	91.2
1 h	40.2	94.6	66.8	91.7
2 h	46.6	94.8	73.2	92.1
6 h	56.5	95.7	82.5	92.4
24 h	68.3	95.8	90.0	92.8

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* For references to previous research, see Ref. 2.

concluded, on the basis of the results of Schlatter.[6] that the initial isomer distribution of *t*-butyltoluene consisted of 7% *m*- and 93% *p*-isomers. Steric hindrance prevents the formation of the *o*-isomer. Usually, in the alkylation and especially transalkylation reaction conditions, subsequent or concurrent isomerization of the reaction mixture takes place and the higher *m*-isomer contents are observed.

However, in the present case, the *t*-butyltoluene produced by transbutylation from di-*t*-butylanisole maintains a high *p*-isomer content throughout the reaction, and there is no sign of secondary reactions, such as isomerization and disproportionation. A slight increase in the *p*-isomer content toward the end of the reaction may be due to further *t*-butylation of *m*-*t*-butyltoluene, forming 3,5-di-*t*-butyltoluene. A low reaction temperature and a low catalyst concentration favor the high *p*-isomer content.

TABLE 3. BUTYLATION OF BENZENE WITH DI-*t*-BUTYLANISOLE AT 20 °C $AlCl_3$ 0.02 mol

Time	Reaction products mol %				
	Benzene	*t*-Butylbenzene			*p*-Isomer % in Dibutylbenzene
		mono-	*m*-di-	*p*-di	
5 min	96.1	2.0	0.2	1.7	90
20 min	92.8	2.7	0.4	4.1	91
40 min	90.6	2.8	0.6	6.0	91
1.5 h	87.4	2.8	0.7	9.1	93
3 h	83.3	4.1	0.9	11.7	93
24 h	73.5	3.0	1.5	22.0	94
120 h	59.4	3.0	2.4	35.2	94

Butylation of Benzene: The results were shown in Table 3. The content of di-*t*-butylbenzenes increased with time, whereas the *t*-butylbenzene content remained almost constant. These results were realized on the assumption that the *t*-butylbenzene initially formed is more reactive than benzene and that the transbutylation of benzene by di-*t*-butylbenzene did not occur.

TABLE 4. BUTYLATION OF ALKYLBENZENE WITH DI-*t*-BUTYLANISOLE AT 25 °C $AlCl_3$ 0.01 mol

Time	Ethylbenzene		Isopropylbenzene		*t*-Butylbenzene	
	Conversion (%)	*p*-isomer (%)	Conversion (%)	*p*-isomer (%)	Conversion (%)	*p*-isomer (%)
5 min	18.8	94.0	19.8	92.0	15.9	93.0
10 min	25.7	94.0	26.0	93.0	21.1	92.5
30 min	35.4	94.6	36.3	93.0	30.2	93.0
1 h	41.2	94.6	41.6	93.3	34.9	93.5
2 h	47.0	94.5	47.8	93.5	40.7	93.5
6 h	55.7	94.8	56.3	93.6	50.4	93.4
24 h	67.0	94.9	67.8	93.3	62.8	93.5

Butylation of Ethyl-, Isopropyl-, and t-*Butylbenzenes*: The results are shown in Table 4. In the course of the reaction, there was no sign of either disproportionation of ethyl- or isopropylbenzene, or isomerization of butylated products.

TABLE 5. REACTION OF TOLUENE WITH *p*-*t*-BUTYLANISOLE AT 25 °C $AlCl_3$ 0.01 mol

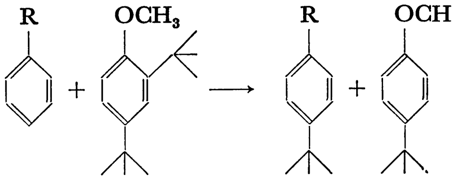
Time	Butyltoluene yield (mol %)	Composition of anisole deriv. (mol %)		
		Anisole	*p*-*t*-Bu-	2,4-(*t*-Bu)$_2$-
20 min	0	2	97.5	1.3
30 min	0	1.9	96.1	2.0
2 h	0	1	95.6	2.2
45 h	6.4	10.9	84.6	4.5

Reaction of Toluene with p-t-*Butylanisole*: The results were shown in Table 5. *t*-Butylation of toluene by *p*-*t*-butylanisole did not occur. Instead, disproportionation of *p*-*t*-butylanisole was observed. Formation of *t*-butyltoluene after 45 h was considered to be the result of trans-*t*-butylation by 2,4-di-*t*-butylanisole.

Thus the *t*-butyl group of the ***para*** position to the methoxy group did not participate in this transbutylation.

Furthermore, confirmation that the *t*-butyl group of the ***ortho*** position transfers to the hydrocarbons was obtained by the result that 4-methyl-2-*t*-butylanisole reacts with toluene to form *t*-butyltoluene and 4-methylanisole. This result will be reported elsewhere.

Therefore, the trans-*t*-butylation of aromatic hydrocarbons with 2,4-di-*t*-butylanisole is shown by the following reaction.



Competitive Trans-t-*butylation*: The results of the competitive *t*-butylations of benzene and toluene are shown in Table 6. When the amount of $AlCl_3$ catalyst was less than 1/2 mol to di-*t*-butylanisole, the competitive reaction proceeded normally. However, when an equimolar amount of a catalyst for di-*t*-butylanisole was used, secondary reactions took place and the apparent k_T/k_B value decreased.

Olah *et al.*[7] have investigated the Friedel-Crafts *t*-butylation of benzene and methylbenzenes with *t*-butyl bromide and with isobutylene. They pointed

TABLE 6. COMPETITIVE *t*-BUTYLATION OF BENZENE AND TOLUENE

Cat. mol ratio	0.1		0.5		1.0	
Time	k_T/k_B	*p*-Isomer in *t*-Bu-toluene	k_T/k_B	*p*-Isomer in *t*-Bu-toluene	k_T/k_B	*p*-Isomer in *t*-Bu-toluene
2 min	24.2		21.1	94.7	15.0	90.3
10 min	23.9	94.3	21.0	93.3	11.3	87.8
30 min	23.1	94.3	22.1	93.5	9.6	85.8
1 h	24.0	94.4	21.6	93.2	8.3	84.2
2 h	23.7	94.5	21.8	93.2	7.0	80.5
24 h	23.9	94.7			2.8	51.7
48 h	23.7	94.7				
	24.0±0.7		21.6±0.5			

Table 7. Competitive *t*-butylation of benzene and C_8 aromatics

Aromatic	k_{Ar}/k_B		
	This work	Olah7)	
	Di-*t*-butylanisole	*t*-BuBr	Isobutylene
Benzene	1.00	1.00	1.00
Toluene	24.0	16.6	15.2
o-Xylene	136	44.3	47.8
m-Xylene	2.2	2.54	3.82
Ethylbenzene	22		

out that secondary isomerization occurred in the *t*-butylation conditions reported by Brown,8) and found that k_T/k_B of the *t*-butylation was 14—16 for non-isomerized conditions. A higher k_T/k_B value (24) was observed in the trans-*t*-butylation with di-*t*-butylanisole.

The competitive *t*-butylation of toluene and C_8 aromatics was also carried out. The data obtained are summarized and compared with the results of Olah in Table 7.

From the data it is seen that the trans-*t*-butylation with di-*t*-butylanisole is the most selective *t*-butylation.

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