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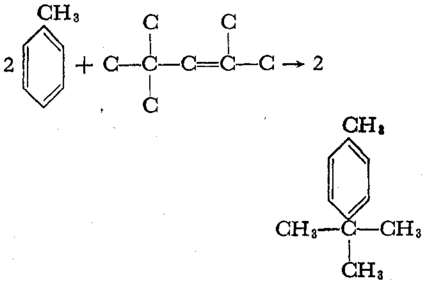
Production of *tert*-Butyltoluene by Depolyalkylation

Boron fluoride monohydrate is a new and effective catalyst for preparing *tert*-butyl derivatives by depolyalkylation of aromatics with diisobutylene. Neither time nor temperature affected the reaction of diisobutylene with toluene within the ranges studied. Reaction was essentially complete at 10° to 40° C. in less than 30 minutes. Higher yields of predominantly para isomers were obtained after catalyst had been re-used or modified by addition of diolefins or other reagents. Depolyalkylation using boron fluoride monohydrate catalyst may be used to make *tert*-butyl aromatic chemicals. High yields, rapid reaction, and predominance of para isomer should be a distinct advantage over Friedel-Crafts alkylation catalysts

Depolyalkylation reactions involving diisobutylene and a variety of aromatic hydrocarbons were extensively investigated. Most of this work dealt with the reaction of toluene and diisobutylene to produce *tert*-butyltoluene. Boron fluoride monohydrate ($BF_3.H_2O$) was found to be an unusually effective catalyst. Under proper conditions, yields were nearly quantitative and only small quantities of the di-*tert*-butyl derivatives and octyltoluenes were formed. Several other olefin polymers were investigated but none was found as good a source of *tert*-butyl ions as diisobutylene.

Production of *tert*-butyl aromatics has been the subject of several reviews. The latest (*9*) compares various alkylating agents, including diisobutylene, and many different catalysts. Use of hydrofluoric acid was reported in 1939 (*1*). Recently Proell and Adams (*6*, *7*) described alkane sulfonic acids as catalysts for this reaction. Probably the first reference to the reaction of toluene with diisobutylene to produce *tert*-butyltoluene was by Noelting (*5*) in 1921; he used ferric and aluminum chlorides as catalysts. However, the term "depolyalkylation" is credited to Ipatieff and Pines (*2*).



The depolyalkylation reaction does not predominate with most acid catalysts. Intact alkylation (*8*) with diisobutylene yields an "octyltoluene"—mainly, 2,2,4-trimethyl-4-(*p*-tolyl)-pentane—whereas depolyalkylation produces mono-*tert*- and 3,5-di-*tert*-butyltoluene. By proper choice of catalyst and conditions, either depolyalkylation or intact alkylation can be made to predominate. With a boron fluoride monohydrate catalyst under the conditions reported, depolyalkylation occurs almost to the exclusion of intact alkylation. Earlier (*3*), the authors reported the effectiveness of this catalyst for dehydroalkylation of aromatics with isoparaffins.

Catalyst and Reactants

The boron fluoride monohydrate catalyst was prepared by passing anhydrous boron trifluoride (Harshaw Chemical Co.) into distilled water for 16 hours at temperature controlled at about 35° C. The resultant complex was a heavy, fuming liquid having a specific gravity of 1.76 at 25° C. The weight increase due to boron fluoride absorption represented a 78.2 weight % concentration of boron fluoride in the final complex; analysis showed 76.5 weight %. These figures approximate the 79.1 weight % required for a 1 to 1 molar ratio of boron fluoride to water.

Diisobutylene was obtained from the Enjay Co., triisobutylene from the Atlantic Refining Co., and tripropylene (nonene) from the American Oil Co. The benzene and toluene were standard nitration-grade materials. *m*-Xylene (95%) was obtained from the Oronite Chemical Co., and *o*-xylene (95%) from the Phillips Petroleum Co.

Typical Experimental Procedure

As the depolyalkylation reaction is highly exothermic, a 2-liter, cylindrical glass reactor, equipped with an internal cooling coil, was used in most of the runs. The toluene (or other aromatic) and catalyst were charged to the reactor in a ratio of 7 to 1 by volume. The diisobutylene (or other olefin polymer) was added to the reactor from a dropping funnel, in a ratio of 1 mole of diisobutylene to 2 moles of aromatic. In a typical run 7 moles (644 grams) of toluene and 190 ml. (335 grams) of boron fluoride monohydrate were charged to the reactor and 3.5 moles (403 grams) of diisobutylene was added at a rate of 20 grams per minute with vigorous stirring. The temperature was held at 33° to 36° C. by circulating cold water through the internal cooling coil. At the end of the desired reaction time (30 minutes in most cases), the hydrocarbon product was separated by decantation, washed with water and 10% sodium hydroxide, and dried over calcium chloride. The dried product was fractionated on a 3 foot × 25 mm. Podbielniak Hypercal column at 10 to 1 reflux ratio. Typical yields of the fractions and infrared analyses are shown in Table I. Nearly complete conversion of toluene and diisobutylene was obtained, the major product being *tert*-butyltoluene.

Experimental Results

Effect of Reaction Conditions. REACTION TIME. A series of runs was made to study the effect of reaction time on yields and product distribution for the reaction of diisobutylene and toluene, with boron fluoride monohydrate catalyst (Table II). The depolyalkylation reaction proceeds rapidly.

REACTION TEMPERATURES. The effect of reaction temperature was studied over the range of 0° to 110° C. Table III shows a slight advantage for the lower temperatures. It is concluded that with a fresh catalyst, temperature changes in this range have little effect on conversion or product distribution.

Effect of Catalyst Age on Yields and Product Distribution. A series of seven runs was made, starting with a fresh batch of boron fluoride monohydrate catalyst, and re-using the catalyst from run to run throughout the series (Table

Table I. Fractionation of Products from Typical Depolyalkylation Run Shows Nearly Complete Conversion of Toluene and Diisobutylene

Cut No.	Boiling Range, ° C.	Reaction Product, Wt. %	Composition, Wt. % (Infrared Analyses)
1	IBP-93	0.5	...
2	93–116	8.6	82.8% toluene
3	116–185	0.5	...
4	185–204	74.2	72% *p-tert*-butyltoluene 28% *m-tert*-butyltoluene
5	204 C+	15.1	43% 3,5-di-*tert*-butyltoluene

Table II. Reaction of Toluene with Diisobutylene Is Essentially Complete in 7 Minutes

Reaction temperature. 32–37° C. Toluene-diisobutylene. 2/1 M. Total hydrocarbon–$BF_3.H_2O$ catalyst. 7/1 volume

	Reaction Time, Minutes			
	7	32	180	300
Yields, mole % on toluene reacting				
tert-Butyltoluene	84.9	85.9	82.0	77.9
3,5-Di-*tert*-butyltoluene	3.0	5.5	4.7	7.8
Toluene reacting, %	85.0	88.5	88.3	93.0

Table III. Temperature Has Little Effect on Reaction of Toluene and Diisobutylene

Reaction time. 150 minutes. Mole ratio toluene/diisobutylene. 2/1. Volume ratio total hydrocarbon/$BF_3.H_2O$. 7/1

	Reaction Temperature, ° C.				
	0–5	33–36	57–60	69–72	100–110
Toluene reacting, %	86.4	87.5	86.5	86.1	77.4
Yields, mole % on toluene reacting					
tert-Butyltoluene	82.0	86.5	84.3	85.8	84.5
3,5-Di-*tert*-butyltoluene	0.8	5.1	4.8	6.1	1.2
Actual product distribution[a], wt. % of total product					
IBP-121° C. (toluene cut)	8.9	9.4	10.5	10.2	14.6
121–185° C.	0.4	0.5	0.4	0.6	0.6
185–204° C. (*tert*-butyltoluene cut)	74.9	76.1	72.6	75.1	69.0
204° C. + (3,5-di-*tert*-butyltoluene and diisobutylene polymers)	15.8	14.0	16.5	14.1	15.8
	100.0	100.0	100.0	100.0	100.0

[a] From Hypercal distillation of total product at 10/1 reflux ratio.

Table IV. Product with Aged Catalysts Was Predominantly Para Isomer

Reaction temperature. 33–36° C. Reaction time. 170–190 minutes. Mole ratio toluene-diisobutylene. 2/1. Initial volume ratio total hydrocarbon/$BF_3.H_2O$. 7/1

	Successive Runs Re-using Same Catalyst						
	1	2	3	4	5	6	7
Toluene reacting, %	91.7	91.5	94.0	94.3	94.6	95.5	96.0
Yields, mole % on toluene reacting							
tert-Butyltoluene	83.6	86.8	89.2	89.5	90.8	91.8	91.6
3,5-Di-*tert*-butyltoluene	7.6	5.7	4.3	3.6	2.6	2.0	1.4
Isomer distribution, wt. %							
p-tert-Butyltoluene	59	59	69	71	75	80	84
m-tert-Butyltoluene	41	41	31	29	25	20	16

IV). As the catalyst "aged," yields of *tert*-butyltoluene increased from 83.6 to 91.6%, while yields of 3,5-di-*tert*-butyltoluene decreased from 7.6 to 1.4%. Per cent toluene reacting increased from 91.7 to 96.0%, in going from the first to the seventh run. The amount of para isomer in the *tert*-butyltoluene fraction consistently increased as the catalyst aged. With fresh catalyst, the *tert*-butyltoluene product was 59% para and 41% meta isomer, but as the catalyst aged, the para content increased to 84% in the seventh run. The improved performance of the aged catalyst is undoubtedly due to the accumulation of conjunct polymers in the catalyst phase.

It appeared that the presence of the para isomer in increased amounts was the key to the higher yields of mono-*tert*-butyltoluene. The *tert*-butyl group is hindered sterically from entering an aromatic ring in a position ortho to another alkyl group. As the product from the use of a fresh boron fluoride monohydrate catalyst was approximately a 60/40 mixture of the para and meta isomers, it is postulated that the entering *tert*-butyl group attached in the para position and was then isomerized to some extent to the meta position by the highly active fresh catalyst. As the *m-tert*-butyltoluene can react further with another *tert*-butyl group to form 3,5-di-*tert*-butyltoluene, the yield of mono-*tert*-butyltoluene was reduced accordingly. As the catalyst aged and the content of soluble oils was built up, its isomerization ability was lessened, and less of the para isomer was converted to the meta isomer. The product with the aged catalyst was predominantly (84%) the para isomer, supporting the view that the *tert*-butyl group first enters in the para position (Table IV).

Isomerization Activity of Boron Fluoride Hydrate Catalysts. To substantiate this isomerization hypothesis, a sample (86.5 grams) of *p-tert*-butyltoluene, containing 93.0 weight % para isomer and 3.0 weight % meta isomer, was mixed for 2 hours with fresh boron fluoride monohydrate (50 ml.) catalyst at 30° C. Another sample was treated under the same conditions with an aged boron fluoride monohydrate catalyst from a series of *tert*-butyltoluene preparations (such as described in Table IV). The products were fractionated and analyzed by infrared. Table V shows that the fresh catalyst caused isomerization and disproportionation of the *tert*-butyltoluene; the used catalyst did not. Although the used catalyst had no isomerization activity, it possessed sufficient activity to catalyze the depolyalkylation effectively. This was demonstrated in another experiment, where used catalyst was employed for the depolyalkylation of toluene with diisobutylene. An 89.0 mole % yield of *tert*-butyltoluene (90% para isomer) based on toluene reacting was obtained; 82.0% of the toluene was converted.

Catalyst Life Study. In view of the high yield of *tert*-butyltoluene produced with boron fluoride monohydrate (Table IV), a life study was made. The results of 28 successive runs with a single batch of catalyst are summarized in Table VI. A reaction time of 25 minutes was used, compared to the long reaction time (170 to 190 minutes) in the runs reported in Table IV. A higher content (72%) of *p-tert*-butyltoluene was obtained in the first run with the fresh catalyst than in the previous series.

A maximum yield of 90% *tert*-butyltoluene was reached after about six runs. The catalyst activity remained at a high level for about 20 successive runs, then dropped rapidly. The spent boron fluoride hydrate catalyst from this series contained 15.20% soluble oils (conjunct polymers) and 65.70% boron fluoride.

Yield was 10.2 gallons of *tert*-butyltoluene per pound of boron fluoride used in this catalyst life study. The spent catalyst could probably be regenerated by one of several methods for separating excess acid oils. In one such experiment, the spent catalyst was diluted

Table V. Fresh Catalyst Caused Isomerization and Disproportionation of *p-tert*-Butyltoluene, Used Catalyst Did Not

(Weight per cent)

		Product after Treatment[a]	
	Charge	Fresh catalyst	Used catalyst
Toluene	**None**	**2.9**	**None**
***p-tert*-Butyltoluene**	**93.0**	**46.0**	**93.0**
***m-tert*-Butyltoluene**	**3.0**	**26.0**	**3.0**
3,5-Di-*tert*-butyltoluene	**None**	**16.3**	**None**

[a] 2 hours at 30° C.

Table VI. Catalyst Life Study Shows High Yields for 16 Consecutive Runs

Reaction temperature. 33–36° C. Reaction time. 25 minutes. Mole ratio toluene-diisobutylene. 2/1. Initial volume ratio of hydrocarbon/$BF_3.H_2O$. 7/1

	Successive Runs Re-using Same Catalyst						
	1	6	11	16	21	26	28
Toluene reacting, %	**88.5**	**95.0**	**90.5**	**77.9**	**61.8**	**23.2**	**<10**
Yields, mole % on toluene reacting							
***tert*-Butyltoluene**	**85.8**	**90.1**	**87.8**	**91.0**	**83.5**	**61.4**	
3,5-Di-*tert*-butyltoluene	**5.5**	**1.3**	**0.25**	**None**	**None**	**None**	
Isomer distribution, wt. %							**No reaction**
***p-tert*-Butyltoluene**	**72**	**84**	**90**	**92**	**93**	**95**	
***m-tert*-Butyltoluene**	**28**	**16**	**10**	**8**	**7**	**5**	

Table VII. Catalyst Modification Increases the Yield of Para Isomer Depolyalkylation in the Toluene with Diisobutylene

Reaction temperature. 30–40° C. Reaction time. 60 minutes

	Run				
	A	B	C	D	E
	Fresh $BF_3.H_2O$	Modified Boron Fluoride Hydrate Catalysts			
Catalyst composition, wt. %					
BF_3	**78.7**	**67.5**	**67.5**	**67.5**	**74.5**
H_2O	**21.3**	**32.5**	**18.3**	**18.3**	**25.5**
Modifier	**None**	**Additional water**	**14.2 Acetone**	**14.2 2,4-Dimethyl-1,3-hexadiene**	**Includes acid oils from 11 runs**
Yields, mole % on toluene reacting					
***tert*-Butyltoluene**	**83.6**	**73.1**	**85.0**	**89.3**	**87.8**
3,5-Di-*tert*-butyltoluene	**7.6**	**0.0**	**0.0**	**0.3**	**0.25**
Toluene reacting, % of charge	**91.7**	**20.0**	**66.1**	**90.6**	**90.5**
Isomer distribution, wt. %					
***p-tert*-Butyltoluene**	**59**	**95**	**94**	**92**	**90**
***m-tert*-Butyltoluene**	**41**	**5**	**6**	**8**	**10**

with 20% water to "spring" the bulk of the acid oils. After refortification with boron fluoride, the catalyst was equivalent to fresh catalyst.

Modification of Catalyst. The marked effect of catalyst age on the ratio of para-meta isomers in the product, and on yields, led to a study of methods of modifying or pretreating the boron fluoride hydrate catalyst to improve its performance. A quantity of the monohydrate was prepared which contained 78.7 weight % boron trifluoride. A portion of this boron fluoride monohydrate was used as catalyst in a toluene-diisobutylene depolyalkylation run to provide a basis of comparison. Three other portions of the boron fluoride monohydrate were diluted to 67.5 weight % boron fluoride content with water, acetone, and 2,4-dimethylhexadiene-1,3, respectively, and similar depolyalkylation runs were made. Data in Table VII compare results with those obtained with a partially spent boron fluoride hydrate catalyst used in 11 consecutive runs in the previous study.

The data in the first column (run A) in Table VII are typical of fresh boron fluoride monohydrate (78.7% boron fluoride) catalyst. Dilution with water, from 78.7% boron fluoride content down to 67.5% rendered the catalyst almost inactive for depolyalkylation (run B); this 67.5% catalyst, which contains 1 mole of boron fluoride per 1.81 moles of water, caused only 20% of the toluene to react. However, the *tert*-butyltoluene produced was predominantly (95%) the para isomer. This indicates that dilution of the boron fluoride content of the catalyst practically eliminates its isomerizing activity. The acetone-modified catalyst (run C), containing about 14% acetone, was more active than the catalyst diluted with water to the same boron fluoride content. With the acetone-modified catalyst, 66% of the toluene reacted, and again the product contained a predominance (94%) of the para isomer, showing little isomerization. Virtually no 3,5-di-*tert*-butyltoluene was produced with either of these catalysts.

Catalyst D, modified with dimethylhexadiene, gave high yields of *tert*-butyltoluene; 90.6% of the toluene reacted to give predominantly the para isomer. The results with this catalyst practically duplicated those obtained with aged catalyst E from the eleventh run of the catalyst life study. The latter can be considered to be modified by build-up of acid-soluble polyolefinic polymers (conjunct polymers), generally formed in acid-catalyzed reactions involving olefins (*4*). Fresh boron fluoride monohydrate gave a somewhat lower yield of *tert*-butyltoluene than the diolefin- or polymer-modified catalysts (D and E), because the fresh catalyst (A) caused formation of 7 to 8% of 3,5-di-*tert*-butyltoluene. The *tert*-butyltoluene product from the fresh boron fluoride monohydrate catalyst contained a high percentage of the meta isomer; modified catalysts yielded mainly para isomer.

Other Catalysts. Other catalysts studied with the toluene-diisobutylene reaction included aluminum chloride, toluenesulfonic acid, 99% sulfuric acid, and 91% "spent" alkylation acid (sulfuric) from a butane-butylene alkylation process (Table VIII). None of these materials approached the effectiveness of boron fluoride monohydrate as catalyst for depolyalkylation. Concentrated sulfuric acid gave rather poor results due to the sulfonation of the aromatics in the reaction mixture. The spent alkylation acid was only slightly better than the concentrated sulfuric acid. Anhydrous toluenesulfonic acid gave the best yield of this group, but was considerably inferior to boron fluoride monohydrate. Aluminum chloride and UOP polymerization catalyst (phosphoric acid on kieselguhr) were about equal, but neither gave yields above 50% of theoretical. Phosphoric acid (85%) gave no reaction under the conditions studied.

A graphic comparison of a number of catalysts for the depolyalkylation reaction is shown in Figure 1. The superiority of boron fluoride monohydrate is striking.

Depolyalkylation Using Other Aromatics and Olefin Polymers. *m*-Xylene, *o*-xylene, benzene, and phenol were also subjected to depolyalkylation with diisobutylene, with boron fluoride monohydrate catalyst. The two xylenes and benzene gave about the same yields as toluene, but no measurable reaction was obtained with phenol (Table IX).

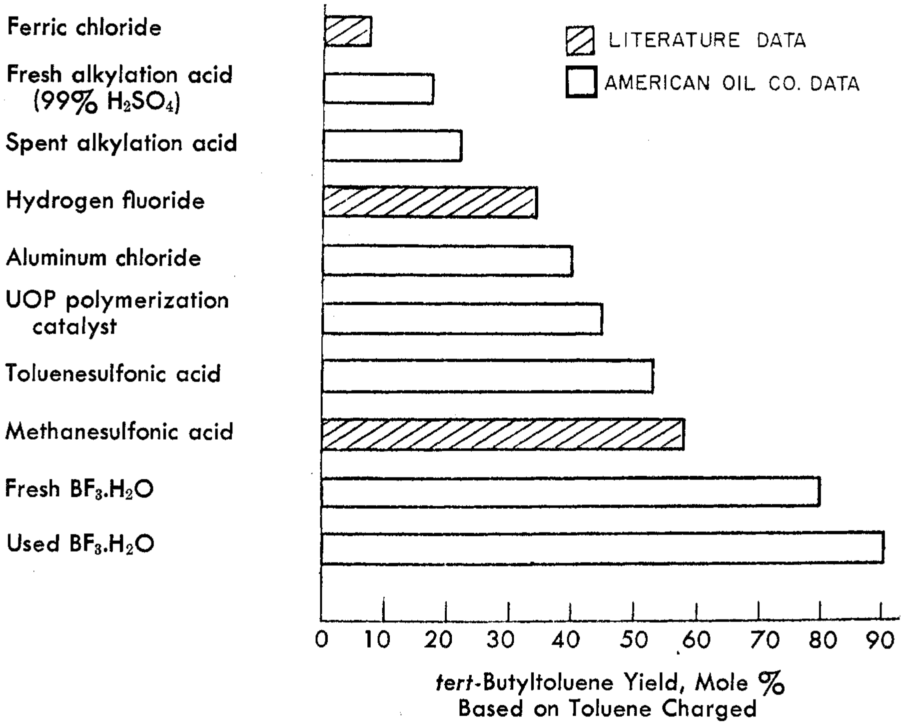


Figure 1. Comparsion of catalysts for depolyalkylation of toluene with diisobutylene

Superiority of boron fluoride is striking

Table X. Depolyalkylation of Toluene with Other Olefin Polymers

	Alkylating Agent	
	Tripropylene	Triisobutylene
Reaction temperature, ° C.	75–80	24–38
Reaction time, minutes	127	54
Toluene-olefin ratio, molar	1.5/1	3/1
Hydrocarbon-catalyst ratio, volume	7/1	7/1
Toluene reacting, %	70.0	85.2
Yields, mole % on toluene reacting		
Isopropyltoluene	1.0[a]	...
***tert*-Butyltoluene**	5.5[b]	77.7[c]
3,5,-Di-*tert*-butyltoluene	...	4.1
Amyltoluene	14.0[d]	...
Total depolyalkylate	20.5	81.8
Nonyltoluene by intact alkylation	51.4[e]	...

[a] Mixture of *p*- and *m*-isopropyltoluene.

[b] 49% *m-tert*-butyltoluene, 51% *p-tert*-butyltoluene.

[c] 62% *p-tert*-butyltoluene, 38% *m-tert*-butyltoluene.

[d] Fraction estimated by infrared examination to be mostly *sec*-amyltoluene.

[e] Calculated from vol. % aromatics in 230° C. + cut.

Tripropylene was tested as a depolyalkylating agent, using toluene and boron fluoride monohydrate. The major reaction was intact alkylation yielding nonyltoluenes. Minor amounts of *tert*-butyltoluene and amyltoluenes were produced (Table X).

The reaction of triisobutylene with toluene gave a 77.7 mole % yield of *tert*-butyltoluene (Table X), only moderately lower than the 85% yields with diisobutylene. In contrast, a methanesulfonic acid catalyst (*6*) gave poor yields of *tert*-butyl aromatics when triisobutylene was used as the alkylating agent, although fairly good yields were obtained from diisobutylene.

Table VIII. Depolyalkylation of Toluene with Diisobutylene with Other Catalysts

No catalyst approached effectiveness of boron fluoride monohydrate

Catalyst	Concd. H_2SO_4 (99%)	91% Used Alkylation Acid (91% H_2SO_4)	$AlCl_3$-Toluene-HCl Complex	Toluene-sulfonic Acid
Ratio toluene-catalyst, volume	4/1	4/1	4/1	4/1
Reaction temp., ° C.	34–37	34–36	34–36	116–120
Reaction time, minutes	180	180	180	180
Toluene-diisobutylene ratio	2/1	2/1	2/1	2/1
Yields, mole % on toluene charged				
***tert*-Butyltoluene**	18.2	22.6	41.7	58.9
3,5-Di-*tert*-butyltoluene	None	None	3.4	0.7
Yields, mole % on toluene reacting				
***tert*-Butyltoluene**	28.4	33.0	65.6	68.0
3,5-Di-*tert*-butyltoluene	None	None	5.4	0.8
Toluene reacting	70.0	69.2	63.5	86.5
Isomer distribution, wt. %				
***p-tert*-Butyltoluene**	98	97	33	92
***m-tert*-Butyltoluene**	2	3	63	8

Table IX. Depolyalkylation of Several Aromatics with Diisobutylene

Xylenes and benzene gave same yields as toluene, but phenol gave no measurable reaction

	Aromatic				
	m-Xylene	*o*-Xylene	Toluene	Benzene	Phenol
Reaction temperature, ° C.	33–36	33–36	35	33–36	45–55
Reaction time, minutes	63	66	60	58	117
Aromatic-diisobutylene, molar	2/1	2/1	2/1	3/1	1/3
Aromatic reacting, %	91.9	91.9	91.7	56.2	...
Yields, mole % on aromatic reacting					
1,3-Dimethyl-5-*tert*-butylbenzene	85.6				No reaction
1,2-Dimethyl-4-*tert*-butylbenzene		84.0			
***tert*-Butyltoluene**			83.6		
***tert*-Butylbenzene**				78.8	
1,3-Di-*tert*-butylbenzene				0.8	
1,4-Di-*tert*-butylbenzene				3.7	
				83.3	

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