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Catalysts for the Hydroalkylation of Benzene, Toluene and Xylenes

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The catalytic hydroalkylation of benzene over palladium and fused salt (NaCl-$AlCl_3$) was examined under hydrogen pressure. The combination catalyst of palladium and fused salt showed good activity for hydroalkylation, providing cyclohexylbenzene as the main product, with a small amount of bicyclohexyl. With 0.24% palladium supported on alumina, suitable reaction conditions were: a temperature of 120—140°, and a reaction time of 5—10 hr in the presence of fused salt (NaCl–$AlCl_3$; molar ratio 1: 1). Under these conditions, the yields of cyclohexylbenzene and bicyclohexyl were 54.7 and 5.1%, respectively. This catalyst system was applied to the hydroalkylation of toluene, xylenes and trimethylbenzenes. Based on the behavior of the fused salt, we suggest that $NaAlCl_4$ represents an active species in the hydroalkylation reaction.

Keywords——hydroalkylation; combination catalyst system; palladium; fused salt; cyclohexylbenzene derivative; bicyclohexyl

Using a bifunctional catalytic system consisting of a hydrogenation catalyst and an alkylation catalyst, we have achieved the one-step synthesis of cyclohexylbenzene from benzene, *i. e.*, "hydroalkylation." For this reaction, two types of catalyst systems can be considered. One is a bifunctional system of Group VIII metal or noble metal catalysts supported on solid acids; the other is a combination of a noble metal catalyst and a Friedel–Crafts catalyst. Many workers[1–4] have used the former type of catalyst to investigate the hydroalkylation of benzene. However, to our knowledge, the use of the latter catalyst system has not yet been reported, since the hydrogenation activity is inhibited by the addition of a small amount of Friedel–Crafts catalysts such as aluminum chloride. We found that the addition of a fused salt, prepared from sodium chloride and aluminum chloride, resulted in excellent alkylation activity without affecting the hydrogenating ability of palladium.

We now report the hydroalkylation of benzene, using a new catalyst system of palladium and fused salt (NaCl–$AlCl_3$), as well as the hydroalkylation of toluene, xylenes and trimethylbenzenes. In addition, the role of the fused salt in the hydroalkylation is discussed.

Results and Discussion

1) Hydroalkylation of Benzene

For this we used 0.24% palladium supported on silica-alumina or alumina in the presence of various alkylation catalysts under hydrogen pressure. The results are shown in Table I.

When Friedel–Crafts catalysts, *e.g.*, $AlCl_3$, $FeCl_3$, $ZnCl_2$ or BF_3, were used with 0.24% palladium on silica-alumina, the hydrogenation of benzene was almost completely inhibited at a reaction temperature of 180°. Furthermore, the yields of cyclohexane and cyclohexylbenzene were poor even at temperatures above 180°. However, when a fused salt (NaCl–$AlCl_3$) was used as the alkylation catalyst instead of aluminum chloride, hydroalkylation proceeded smoothly and the cyclohexylbenzene yield reached 54.7% in the presence of 0.24% palladium-alumina at 140° in 5 hr. Among the chlorides of Li, Na, K, and Cs, sodium chloride gave the highest yield.[5] The effect of the amount of fused salt (NaCl–$AlCl_3$, molar ratio 1: 1) on the yields of cyclohexylbenzene and bicyclohexyl is shown in Table II.

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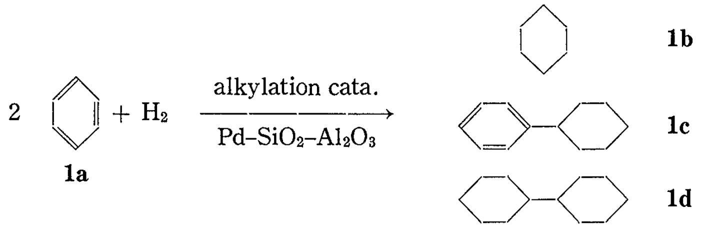
Table I. Hydroalkylation of Benzene in the Presence of Various Alkylation Catalysts and $Pd-SiO_2-Al_2O_3$



Alkylation cata. (g)	Temp. (°C)	Time (hr)	Yield (%) 1c	Yield (%) 1d
$AlCl_3$(0.2)	105	10	0.23	0.04
$FeCl_3$ (0.5)	180	8	0.74	0.06
$ZnCl_2$ (0.5)	170	2.5	0.30	0.02
47% BF_3-ether (0.5)	140	5	0	0
$ZnCl_2$–NaCl–KCl (3.0) (2:1:1 molar ratio)	180	5	0	0
NaCl–$AlCl_3$ (4.0) (1:1 molar ratio)	105	10	20.30	1.20
NaCl–$AlCl_3$ (4.0)[a] (1:1 molar ratio)	140	5	54.70	5.10

Benzene, 30 g; 0.24% $Pd-SiO_2-Al_2O_3$, 1.0g.
[a] 0.24% $Pd-Al_2O_3$, 1.0 g.

Table II. Effect of the Amount of Fused Salt on the Cyclohexylbenzene Yield

NaCl–$AlCl_3$ (g)	Yield (%) 1a	Yield (%) 1b	Yield (%) 1c	Yield (%) 1d
0	Trace	98.4	0	0
2.0	50.4	18.0	30.4	1.1
4.0	42.8	20.4	36.9	0.6
7.0	45.0	22.6	30.8	0.6

Benzene, 30 g; 0.24% $Pd-SiO_2-Al_2O_3$, 1.0 g; NaCl–$AlCl_3$ (1:1); 105°; 5 hr.

When benzene was treated at 105° for 5 hr with 0.24% palladium on silica-alumina in the absence of fused salt, cyclohexane was obtained as the sole product in 98.4% yield. Saturation in the yield of hydroalkylated products was observed at 4 g of fused salt to 1g of the palladium catalyst.

The relation between the reaction time and the cyclohexylbenzene yield is shown in Fig. 1. Cyclohexylbenzene, bicyclohexyl and cyclohexane were obtained as reaction products and no other product was detected at a reaction time exceeding 10 hr. At a reaction temperature of 105° and a reaction time of 10 hr, the yields of cyclohexylbenzene and bicyclohexyl reached 42.3 and 2.1%, respectively, with 1.0 g of 0.24% $Pd-Al_2O_3$ and 4.0 g of fused salt (molar ratio 1:1). Furthermore, the conversion of benzene increased with increasing reaction temperature, while the cyclohexylbenzene yield decreased after reaching a maximum at 140°. Cyclohexylbenzene and bicyclohexyl yields reached maxima of 54.7 and 5.1%, respectively, on reaction at 140° for 5 hr. At higher temperatures, cyclohexane was obtained as the main product. A rise in the reaction temperature promoted both alkylation and hydrogenation; the latter was accelerated to a greater extent than the former at temperatures above 140°.

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2) Hydroalkylation of Toluene

The hydroalkylation of toluene and of a toluene–benzene mixture was also studied under conditions identical to those under which benzene was hydroalkylated. The products obtained with the 1% Pd-clay and fused salt catalysts are summarized in Table III.

In the hydroalkylation of toluene at 80°, two products, 2d and 2e, were obtained in 15.0 and 3.0% yields, respectively. At a reaction temperature of 120°, the yields of **2d** and **2e** increased to 18.6 and 7.3%, respectively. However, at temperature above 150°, so many hydroalkylated products were obtained that quantitative analysis was impossible.

2d and **2e** were separated by a gas chromatography fractionation technique and their structures were assigned on the basis of spectroscopic and elemental analysis data (Table IV). The elemental analysis data showed that **2d** and **2e** had the same formula. However, the ultraviolet spectra (UV) of **2d** and **2e** showed maxima at 266 and 261 nm, respectively; these correspond to *p*- and *o*-isomers as judged by comparison with the spectra of *p*-xylene and *o*-xylene, respectively. The nuclear magnetic resonance (NMR) spectrum of **2d** exhibited a

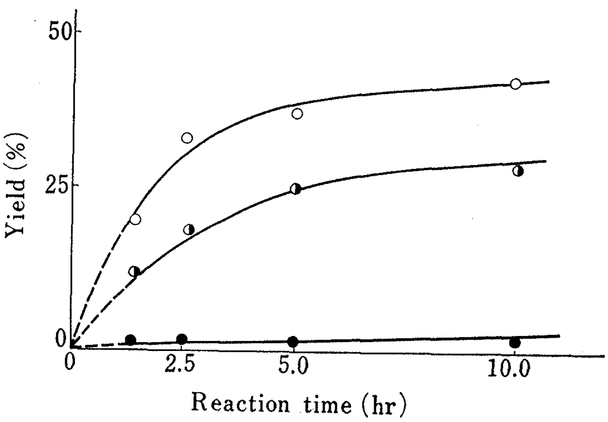
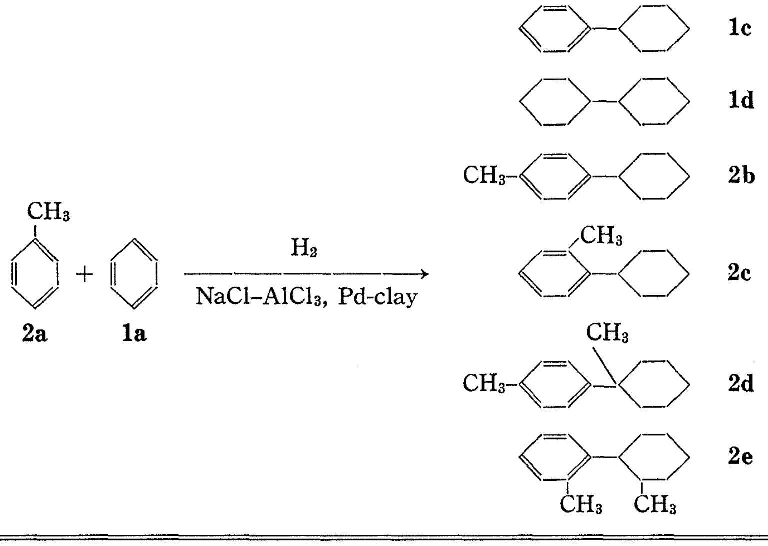


Fig. 1. Relation between the Reaction Time and the Yields of Cyclohexylbenzene and Bicyclohexyl

Benzene, 30 g; 0.24% $Pd-Al_2O_3$, 1.0 g, $NaCl-AlCl_3$ (1: 1), 4.0 g; 105°.

-○- cyclohexylbenzene, -◑- cyclohexane, -●- bicyclohexyl.

Table III. Hydroalkylation of Toluene and of a Toluene–Benzene Mixture (1: 1) in the Presence of $NaCl-AlCl_3$ and Pd



Reactant (g)	Temp. (°C)	Time (hr)	Yield (%)					
			1c	1d	2b	2c	2d	2e
2a+**1a** (18) (15)	80	5	1.5	0	5.2	1.0	2.0	Trace
2a (30)	80	12	0	0	0	0	15.0	3.0
2a	120	12	0	0	0	0	18.6	7.3

1% Pd-clay, 1.0 g; $NaCl-AlCl_3$ (1: 1), 2.0 g.

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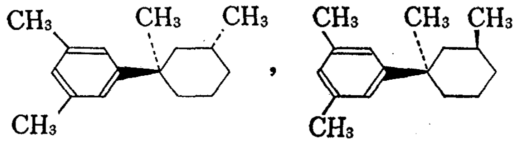
singlet at 0.97 ppm (3H) due to the methyl attached to the *tert*-carbon of the cyclohexyl ring; a multiplet at 1.43 ppm (10H) due to the cyclohexyl moiety; and a singlet at 2.31 ppm (3H), assigned to the methyl on the phenyl ring. On the other hand, the NMR spectrum of **2e** showed a doublet at 0.72 ppm (3H) due to the methyl group attached to the cyclohexyl ring. We[5] previously proposed 4,4′-dimethylcyclohexylbenzene and 4,4′-dimethylbicyclohexyl as the structures of **2d** and **2e**, respectively. However, based on the present results, the structures of the products were unequivocally determined to be 4,1′-dimethylcyclohexylbenzene (**2d**) and 2,2′-dimethylcyclohexylbenzene (**2e**) (Table III). When an equimolar mixture of benzene and toluene was used, *o*-cyclohexyltoluene and *p*-cyclohexyltoluene were obtained as the major products.

TABLE IV. Physical Properties of **2b**—**2e**

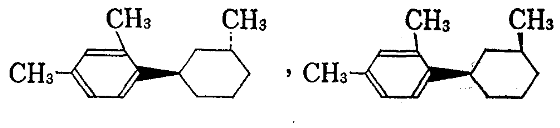
Compd. No.	Formula	Analysis (%) Calcd (Found) C	H	UV(nm) λ_{max}^{EtOH}	NMR (ppm)
2b	$C_{13}H_{18}$	89.66 (89.78	10.34 10.22)	265	1.41(m) 2.33(s)
2c	$C_{13}H_{18}$	89.66 (89.75	10.34 10.25)	260	1.45(m) 2.30(s)
2d	$C_{14}H_{20}$	89.36 (89.53	10.64 10.46)	266	0.97(s) 1.43(m) 2.31(s)
2e	$C_{14}H_{20}$	89.36 (89.45	10.64 10.25)	261	0.72(d) 1.43(m) 2.37(s)

3) Hydroalkylation of Xylenes

Similar reactions were performed with *m*-xylene; the results are shown in Table V. When the molar ratio of NaCl: $AlCl_3$ was 1.5: 1.0, two products, **3b**-2 and **3b**-3, were obtained. Based on their physical properties (Table IX), compounds **3b**-2 and **3b**-3 are identical, suggesting that they are *cis*- and *trans*-forms. The yield of hydroalkylated products increased with increase in the aluminum chloride content in the fused salt. By the use of NaCl–$AlCl_3$ (molar ratio 1: 1) fused salt, *cis*- and *trans*-2,4,3′-trimethylcyclohexylbenzene (**3b**-5, **3b**-6) were obtained. These findings indicate that the methyl group was eliminated. The higher the aluminum chloride content in the fused salt, the more complex were the products, since elimination of the methyl group and hydroalkylation in another position took place. In contrast to the hydroalkylation of toluene, that of *m*-xylene does not follow *ortho*-*para* orientation, nor is it affected by the blocking effect of the methyl groups or steric hindrance.



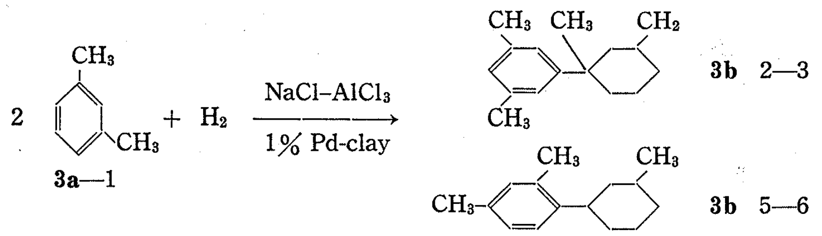
3b−2 and **3b**−3



3b−5 and **3b**−6

Table VI shows the results of hydroalkylation of *o*-, *m*- and *p*-xylene with 1.0% Pd-clay and fused salt (NaCl–$AlCl_3$, 1.5: 1.0) at a reaction temperature of 100°. When *o*-xylene was used, 3,4,1′,2′-tetramethylcyclohexylbenzene (**3b**-1) was formed as the sole hydroalkylated product and *cis* and *trans* forms could not be separated by gas chromatography on 20% silicone

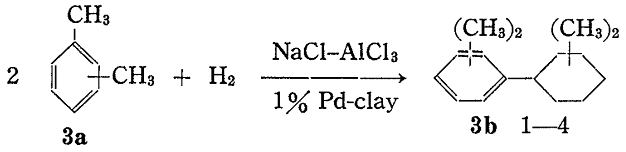
Table V. Hydroalkylation of *m*-Xylene in the Presence of NaCl–AlCl$_3$ and Pd-clay



NaCl–AlCl$_3$ (Molar ratio, g)	Time (hr)	Yield (%)			
		3b-2	3b-3	3b-5	3b-6
1.5 : 1 1.0	12	12.9	5.7	0	0
1.3 : 1 1.0	12	15.9	12.2	7.7	6.9
1:1 2.0	8	14.2	7.1	10.0	11.1

m-Xylene, 30 g; 1% Pd-clay, 1.0 g; 100°.

Table VI. Hydroalkylation of Xylenes in the Presence of NaCl–AlCl$_3$ and Pd-clay



Reactant (3a)	Products		
	Compd. No.	CH$_3$ position	Yield (%)
o-Xylene	**3b**-1	3, 4, 1′, 2′—	16.6
m-Xylene	**3b**-2	3, 5, 1′, 3′—	5.7
	3b-3	3, 5, 1′, 3′—	12.9
p-Xylene[a]	**3b**-4	2, 5, 2′, 5′—	18.4

Xylene, 30 g; NaCl–AlCl$_3$ (1.5: 1), 1.0 g; 1% Pd-clay, 1.0 g; 100°; 12 hr;
a) 8 hr.

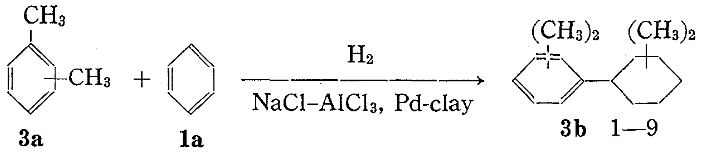
DC-550; 2 m. In the hydroalkylation of *p*-xylene, 2,5,2′,5′-tetramethylcyclohexylbenzene (**3b**-4) was obtained.

The hydroalkylation of xylene–benzene mixture (molar ratio 1: 1) was carried out under conditions identical to those used in the hydroalkylation of xylenes alone (Table VII). Cyclohexylxylenes were the main products; a small amount of cyclohexylbenzene and a trace amount of tetramethylcyclohexylbenzene were detected, suggesting that the formation of cyclohexylxylenes is the result of an attack by the cyclohexyl cation on xylenes, and that the cyclohexyl cation is more reactive than the dimethylcyclohexyl cation. Table VIII shows the effect of reaction temperature on the hydroalkylation of an *o*-xylene–benzene mixture. The reaction occurred at temperatures above 80°. The yield of 3,4-dimethylcyclohexylbenzene (**3b**-7) was maximal (18.74%) at 120°. At a temperature of 160°, the formation of cyclohexylbenzene and bicyclohexyl was marked. As in the case of toluene, when the reaction temperature exceeded 160°, qualitative and quantitative analyses were impossible due to the complexity of the products.

4) Hydroalkylation of Trimethylbenzenes

Mixtures of trimethylbenzene–benzene were also hydroalkylated under similar conditions (Table X); analytical data are presented in Table XI. The hydroalkylation of trimethyl-

Table VII. Hydroalkylation of Xylene–Benzene Mixtures in the Presence of NaCl–$AlCl_3$ and Pd-clay



Reactant	Products Compd. No.	 CH_3 position	 Yield (%)
1a+*o*-xylene	**1c**	—	2.4
	3b-1	3, 4, 1′, 2′—	2.4
	3b-7	3, 4—	9.0
1a+*m*-xylene	**1c**	—	1.5
	3b-2	3, 5, 1′, 3′—	2.1
	3b-8	3, 5—	15.0
1a+*p*-xylene	**1c**	—	
	3b-4	2, 5, 2′, 5′—	2.9
	3b-9	2, 5—	Trace
			5.8

Xylene, 20 g; benzene, 15 g; NaCl–$AlCl_3$ (1.3: 1), 1.0 g; 1% Pd-clay, 1.0 g; 80°; 5 hr.

Table VIII. Hydroalkylation of *o*-Xylene–Benzene Mixture at Various Reaction Temperatures

Temp. (°C)	Yield (%) **1c**	 **1d**	 **3b**-1	 **3b**-7
80	2.40	0	2.40	9.00
120	3.65	0.22	1.49	18.74
160	13.60	3.33	0.28	13.33

o-Xylene, 20 g; benzene, 15 g; NaCl–$AlCl_3$ (1.3: 1), 1.0 g; 1% Pd-clay, 1.0 g; 5 hr.

benzenes gave cyclohexyltrimethylbenzenes (**4b** 1—3); the order of reactivity was 1,2,3-trimethylbenzene, pseudocumene and mesitylene. This order of reactivity is in full agreement with the extents of steric hindrance due to the methyl groups on the phenyl ring. In the cases of pseudocumene and mesitylene, hydroalkylated products were not obtained in the reaction of the trimethylbenzene alone. On the other hand, 1,2,3-trimethylbenzene provided 2,3,4,1′,2′,3′-hexamethylcyclohexylbenzene (**4b**-4) in 2.1% yield.

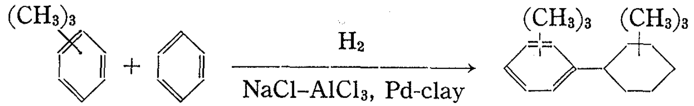
5) Catalytic Activity and Composition of the Fused Salt

Fig. 2 shows the effect of the composition of the fused salt and the NaCl: $AlCl_3$ ratio on the cyclohexylbenzene yield. The hydroalkylation activity increased with increase in the ratio of aluminum chloride to sodium chloride up to 50%, but a further increase in the aluminum chloride content resulted in a decrease of the activity; at an aluminum chloride content of more than 66%, no hydroalkylated products were obtained. Maximum conversion and yield were observed at an aluminum chloride content of 50%. To test whether the aluminum chloride liberated from the fused salt interferes with the hydrogenation on palladium, we qualitatively estimated the solubility of the fused salt in benzene in the presence of 1.0 g of 0.24% palladium-alumina and 4.0 g of fused salt after reaction at 105° for 1 hr. The concentration of chloride ion in benzene was determined by the method of Mohr, by titration with a 0.1 N aqueous solution of silver nitrate. The results are shown in Fig. 3. Although aluminum chloride is soluble in benzene, the fused salt with an aluminum chloride content of up to 50% was almost insoluble. Above an aluminum chloride content of 50%, the chloride ion concentration increased linearly with increase in the aluminum chloride content of the fused salt. These results suggest that if the fused salt contains more than 50% aluminum chloride, it is liberated, resulting in inhibition of the hydrogenation on palladium.

TABLE IX. Physical Properties of **3b** 1—9

Compd. No. (**3b**)	Formula	Analysis (%) Calcd (Found)		UV(nm) $\lambda_{\max}^{\mathrm{EtOH}}$	NMR (ppm)
		C	H		
3b-1	$C_{16}H_{24}$	88.80 (88.14	11.20 11.00)	267.0	0.66(d), 2.30(s) 1.30(s) 1.50(m)
3b-2	$C_{16}H_{24}$	88.80 (88.50	11.20 10.92)	265.0	0.90(d), 2.33(s) 1.10(s) 1.47(m)
3b-3	$C_{16}H_{24}$	88.80 (88.25	11.20 10.75)	264.6	0.92(d), 2.33(s) 1.20(s) 1.56(m)
3b-4	$C_{16}H_{24}$	88.80 (88.52	11.20 11.29)	267.8	0.67(d), 2.30(s) 0.90(d) 1.52(m)
3b-5	$C_{15}H_{22}$	89.10 (87.32	10.90 11.90)	267.2	1.00(d) 1.60(m) 2.35(s)
3b-6	$C_{15}H_{22}$	89.10 (87.86	10.90 11.61)	266.6	0.95(d) 1.55(m) 2.33(s)
3b-7	$C_{14}H_{20}$	89.36 (88.97	10.64 10.03)	267.4	1.42(m) 2.34(s)
3b-8	$C_{14}H_{20}$	89.36 (89.26	10.64 10.79)	265.6	1.43(m) 2.28(s)
3b-9	$C_{14}H_{20}$	89.36 (88.94	10.64 11.02)	266.8	1.42(m) 2.32(s)

TABLE X. Hydroalkylation of Trimethylbenzenes in the Presence of NaCl–AlCl$_3$ and Pd-clay



4a **1a** **4b** 1—4

Reactant	Temp. (°C)	Time (hr)	Products		
			Compd. No.	CH_3 position	Yield (%)
1a+1, 2, 3—	90	10	**1c**	—	2.7
			4b-1	2, 3, 4	12.9
1, 2, 3—	100	10	**4b**-4	2, 3, 4, 1′, 2′, 3′—	2.1
1a+1, 2, 4—	100	10	**1c**	—	1.9
			4b-2	2, 4, 5—	4.9
1, 2, 4—	100	10			0
1a+1, 3, 5—	100	12	**1c**	—	0.2
			4b-3	2, 4, 6—	1.0
1, 3, 5—	100	12			0

Trimethylbenzene, 23 g; benzene, 15 g; NaCl–AlCl$_3$ (1.5 : 1), 1.0 g; 1% Pd-clay, 1.0 g.

TABLE XI. Physical Properties of **4b** 1—4

Compd. No. (**4b**)	Formula	Analysis (%) Calcd (Found) C	H	UV(nm) $\lambda_{\max}^{\mathrm{EtOH}}$
4b-1	$C_{15}H_{22}$	89.10 (89.40	10.90 10.91)	266.8
4b-2	$C_{15}H_{22}$	89.10 (88.91	10.90 11.41)	269.8
4b-3	$C_{15}H_{22}$	89.10 (89.17	10.91 11.27)	268.2
4b-4	$C_{18}H_{28}$	88.52 (88.40	11.48 11.64)	267.1

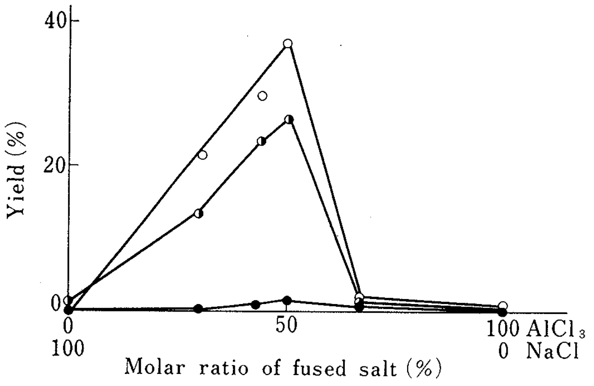


Fig. 2. Effect of the Composition of the Fused Salt on the Cyclohexylbenzene Yield

Benzene, 30 g; 0.24% Pd-Al_2O_3, 1.0 g; NaCl-$AlCl_3$, 4.0 g; 105°; 5 hr.
-○- cyclohexylbenzene, -◑- cyclohexane, -●- bicyclohexyl.

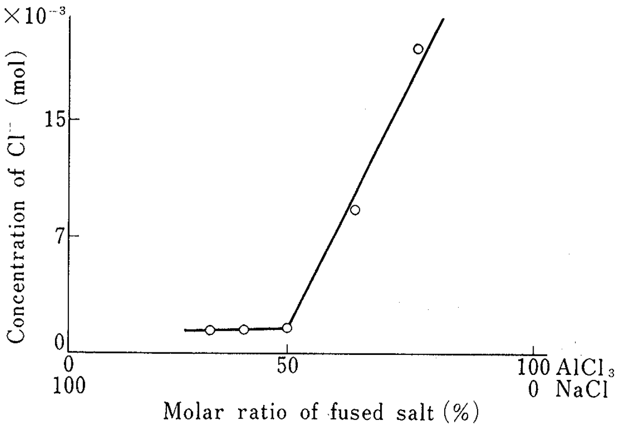


Fig. 3. Concentration of Cl^- in Benzene

Benzene, 30 g; 0.24% Pd-Al_2O_3, 1.0 g; NaCl-$AlCl_3$, 4.0 g; 105°; 1 hr.

To test this hypothesis, we analyzed the structure of the fused salt by determining the X-ray powder patterns of the fused salt at various compositions. Semenenko *et al.*[6] attributed the peaks observed at 16.6° (d=5.32), 24.8° (d=3.58), 28.8° (d=3.09), 30.3° (d=2.948), 31.0° (d=2.88), 35.3° (d=2.541), and 56.0° (d=1.64) to $NaAlCl_4$. Typical X-ray diffraction patterns of fused salt (NaCl–$AlCl_3$, molar ratio 1: 1) are shown in Fig. 4, in which peaks due to NaCl, $AlCl_3$ and $NaAlCl_4$ can be observed. In Fig. 5, the intensity of the $NaAlCl_4$ peaks in fused salt at 34.9° (d=2.569) and 56.8° (d=1.62) is plotted against fused salt composition. With an increase in the aluminum chloride content, the intensity of the $NaAlCl_4$ peaks increased, reaching maximum intensity at an aluminum chloride content of 50%, whereas above 50%, the peaks decreased markedly. As these results coincide with the changes of hydroalkylation activity, we suggest that $NaAlCl_4$ represents an active species in the hydroalkylation reaction.

6) Reaction Scheme

Slaugh and Leonard[1] have proposed a hydroalkylation scheme for benzene over Ni–SiO_2–Al_2O_3. According to these workers, in the hydrogenation of benzene, a cyclohexyl species is first formed on nickel, and it in turn alkylates benzene on an acid site of SiO_2–Al_2O_3. Truffault[7] concluded that cyclohexene and cyclohexadiene are intermediates in the hydroalkylation of benzene over a nickel catalyst in the presence of P_2O_5, since he obtained cyclohexylbenzene and dicyclohexylbenzene as reaction products. In our system, no products related to dicyclohexylbenzene were obtained. A disproportionation between benzene and cyclohexane may

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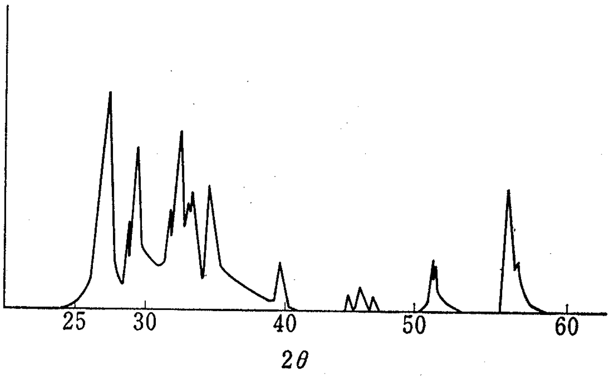

Fig. 4. X-Ray Diffraction Pattern of the Fused Salt (1: 1)

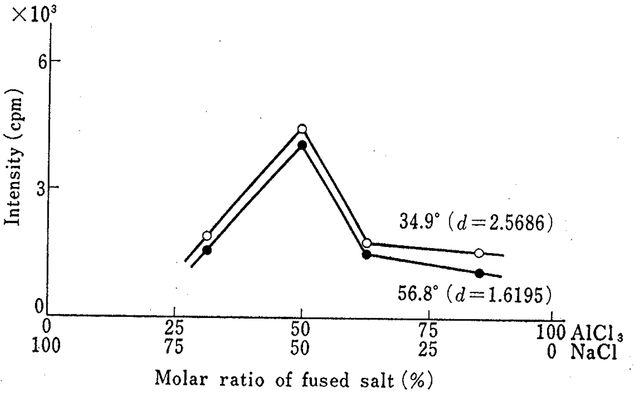

Fig. 5. X-Ray Diffraction Strength of Fused Salt at 34.9° and 56.8°

represent another route for the formation of cyclohexene. To investigate this possibility, we performed disproportionation experiments under the same conditions as hydroalkylation in the absence of hydrogen. If disproportionation occurs, it can be expected that cyclohexene will be formed and will react with benzene to give cyclohexylbenzene. However, at 120° for 18 hr, the yield of cyclohexylbenzene was only 0.3% in the presence of 1.0 g of 0.24% Pd–Al_2O_3 and 4.0 g of fused salt (molar ratio 1: 1), and no trace of cyclohexene or cyclohexadiene was detected. Another possible intermediate is the cyclohexyl cation, formed by the abstraction of a hydride ion from cyclohexane on palladium. However, dehydrogenation to benzene over 0.24% Pd–Al_2O_3 and fused salt failed to occur. Therefore, as already suggested by others[1,2] cyclohexene is the most probable intermediate species in the hydroalkylation of benzene, and it is likely that this electrophilic species is alkylated with benzene on the fused salt. Further experiments using bifunctional catalytic system of palladium and fused salt are in progress in our laboratory with several kinds of aromatic compounds, *e.g.*, aniline and phenol.

Experimental

1) **Preparation of Catalysts**——Fused Salt: Anhydrous aluminum chloride and sodium chloride were introduced into a glass test tube and heat-melted. After cooling at room temperature, the fused compound was crushed and used in powder form.

Palladium Catalysts: The carrier, *e.g.*, alumina, silica-alumina or acid-clay, was dispersed in an aqueous solution of $PdCl_2$–KCl, and the water was evaporated off by heating in a water bath. The resulting powder was calcined at 300—350° for 5 hr.

2) **General Procedure for the Preparation of Cyclohexylbenzene**——Benzene (30 g), 0.24% Pd-Al_2O_3 (1.0 g) and fused salt (NaCl–$AlCl_3$, molar ratio 1: 1, 4.0 g) were placed into a stainless steel autoclave (Sakashita Ltd., SUS-32, 100 ml volume) equipped with a magnetic stirrer (900—1200 rpm). The air in the autoclave was displaced with hydrogen, a pressure of 100—150 kg/cm² was established, and the autoclave was heated at 80—200° for 1—20 hr. The hydrogen was pressurized until hydrogen uptake ceased.

3) **Analysis of Products**——Liquid products were washed with water; oily products were extracted with ether. Ether was removed from the extract by evaporation, and the products were analyzed by gas chromatography (Shimadzu Ltd., type DC-3BF; column packing, 20% silicone DC-550 on Shimalite (80—100 mesh) (2m); frame ionization detector). Hydrogenated products and unreacted benzene were also analyzed by gas chromatography on polyethylene glycol (2m)+apiezone grease (1m) column packing.[8] The products were isolated by fractionation and identified by UV and NMR spectroscopy and elemental analysis. All elemental analysis data are uncorrected. UV spectra were recorded on a Hitachi 556 spectrophotometer; NMR spectra were determined on a Varian EM-390 instrument in $CDCl_3$, with tetramethylsilane as an internal standard. The abbreviations are: s (singlet), d (doublet) and m (multiplet). The X-ray diffraction patterns were measured with a Geigerflex D-3F (Rigaku Denki Ltd., Ni-filtered Cu Kα-radiation).

References and Notes

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