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Hydroalkylation* of Aromatic Compounds†

JAMES J. LOUVAR AND ALFONSO FRANCOY

From the Universal Oil Products Company, Des Plaines, Illinois 60016

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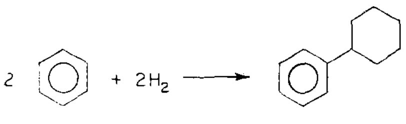
Benzene and toluene, when hydrogenated under certain conditions, yield aromatic substituted alicyclic compounds. If benzene, for instance, is hydrogenated with a Group VIII metal catalyst in the presence of an acid ($SiO_2Al_2O_3$, $AlCl_3$, BF_3, etc.), phenylcyclohexane is found among the hydrogenation products. If the Group VIII metal is deposited on a silica–alumina surface, thereby forming a dual-functional catalyst, hydroalkylation is the major reaction. Toluene, for instance, is nearly quantitatively converted to 1-(*p*-tolyl)- and 1-(*m*-tolyl)-1-methylcyclohexane with a 5% nickel on silica–alumina catalyst and hydrogen. These results demonstrate the dual functionality of the supported catalyst.

INTRODUCTION

Truffault (*1*) reported the isolation of phenylcyclohexane and dicyclohexylbenzene from the hydrogenation of benzene over a nickel catalyst in the presence of P_2O_5. He therefore concluded that cyclohexene and cyclohexadiene were intermediates in benzene hydrogenation. We (*2*) have also found that if benzene is hydrogenated in the presence of nickel and other Group VIII metals and a variety of acid catalysts, $AlCl_3$, BF_3, silica–alumina, etc., phenylcyclohexane is obtained [Eq. (1)].



(Eq. 1)

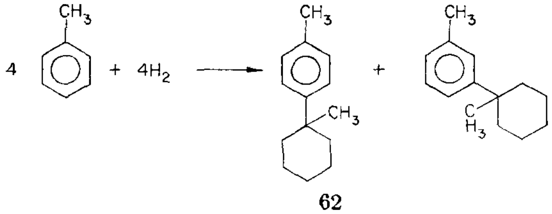
These results have been confirmed by the work of Slaugh and Leonard (*3*).

In the hydrogenation of toluene with the Group VIII metals deposited onto an acidic support, 1-(*p*-tolyl), and 1-(*m*-tolyl)-1-methylcyclohexane are obtained as the major products, Eq. (2). This phenomenon clearly demonstrates the efficient dual functionality which can be built into supported catalysts.

EXPERIMENTAL SECTION

Materials

The catalytic materials were either used directly as received from the supplier or prepared as described below. Platinum oxide, palladium chloride, and 5% palladium on carbon catalysts were obtained from Englehard; copper chromite from Girdler; $AlCl_3$, $AlBr_3$, and P_2O_5 from Sargent; and BF_3 from Matheson. The silica–alumina (75% silica, 25% alumina, ⅛-in. pilled hydrocracking catalyst) and alumina (ABD = 0.5 g/cm³, surface area = 180 m²/g) (*4*) catalyst support materials were obtained from the UOP



(Eq. 2)

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* Hydrogenation-alkylation combination process.

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catalyst manufacturing division, Shreveport, Louisiana. Benzene and toluene were used as received from Merck.

5% Nickel on silica–alumina. Silica–alumina (55 g of 40–60 mesh) was impregnated in a rotary drier with a solution of nickelous nitrate (14.6 g in 100 ml of water). The dried catalyst was calcined for 1 hr at 593°C and reduced in a hydrogen atmosphere at 398°C for 7 hr.

5% Nickel on alumina. Alumina (50 g of 40–60 mesh) was impregnated in a rotary drier with a solution of nickelous nitrate (13.3 g in 100 ml of water). The dried catalyst was calcined for 1 hr at 593°C and reduced in a hydrogen atmosphere for 7 hr at 398°C.

0.375% Palladium on silica–alumina. Silica–alumina (55 g of 40–60 mesh) was impregnated in a rotary drier with a solution of palladium chloride (0.344 g in 100 ml of water containing 1.3 ml of concentrated HCl). The dried catalyst was calcined at 593°C for 1 hr and reduced in a hydrogen atmosphere for 3 hr at 426°C.

0.375% Platinum on silica–alumina. Silica–alumina (22.4 g of 40–60 mesh) was impregnated in a rotary drier with a solution of chloroplatinic acid (3.01 g in 45 ml of water). The dried catalyst was calcined for 1 hr at 593°C and reduced in an atmosphere of hydrogen for 3 hr at 537°C.

5% Nickel, 2.5% arsenic on silica–alumina. Silica–alumina (55 g of 40–60 mesh) was impregnated in a rotary drier with a solution of nickelous nitrate (14.6 g in 100 ml of water). The dried catalyst was calcined for 1 hr at 593°C. This material (15 g) was then impregnated in a rotary drier with a solution of arsenic pentoxide (0.0734 g in 40 ml of water). The dried catalyst was calcined for 1 hr at 593°C and reduced in an atmosphere of hydrogen for 7 hr at 398°C.

5% Nickel, 5% arsenic on silica–alumina. The above described 5% nickel in silica–alumina (15 g) was impregnated in a rotary drier with a solution of arsenic pentoxide (0.1468 g in 40 ml of water). The dried catalyst was calcined at 593°C for 1 hr and reduced in an atmosphere of hydrogen for 3 hr at 398°C.

60% Nickel on kieselguhr. The commercial Harshaw catalyst Ni-104P (20 cc) was reduced at 426°C in an atmosphere of hydrogen and pulverized prior to being used.

Rotating Autoclave Experiments

The hydrogenation catalyst (1–5 g) and the alkylation catalyst (1–5 g), and the aromatic compound (44 g, 0.55 mole) were weighed into an 850 ml glass cylindrical vessel which was placed in a stainless steel autoclave and pressured to 65–100 atm with hydrogen. While being rotated the autoclave was slowly heated until a pressure drop was observed. This temperature was maintained until about one-half the theoretical ΔP (representing the hydrogen required to hydrogenate all the aromatic hydrocarbon present) was obtained and then the autoclave was cooled and depressured. The time requirement ranged from 2 to 6 hr, depending on catalyst activity. The product was filtered to remove the catalyst and the filtrate analyzed by gas-liquid chromatography (GLC).

Parr Apparatus Experiments

These experiments were conducted exactly as described above except that a 500 ml hydrogenation bottle and its contents were pressured to 60 psig with hydrogen after being mounted onto the Parr Apparatus model No. 3910. In those experiments where soluble alkylation catalysts were used the product was water-washed before being analyzed by GLC.

RESULTS AND DISCUSSION

The first phase of this investigation consisted of preliminary experiments involving the hydrogenation of benzene at high pressures in the rotating autoclave with physical mixtures of hydrogenation and alkylation catalysts. The second phase dealt with mixtures of catalytic species but at low pressures in the Parr hydrogenation apparatus. The final phase consisted of a study of the hydrogenation of toluene at low pressures with catalytic Group VIII metals supported on acidic surfaces.

No attempt was made to purify the aromatics, since no distinction was being

TABLE 1

THE HYDROGENATION OF BENZENE WITH MIXTURES OF ALKYLATION AND HYDROGENATION CATALYSTS

Expt. no.	Catalyst (g)		Temp. (°C)	Pressure		Conversion (%) to		
	Alkylation	Hydrogenation		(psig)	Δ (psig/hr)	C_6H_{12}	$C_6H_{11}C_6H_5$	$C_{12}H_{22}$
1	P_2O_5 (2)	60% Ni (2) on kieselguhr	115	1000	54	50	0	0
2	Silica-alumina (1)	Copper chromite (1)	250	1500	160	75	0.1	0.1[a]
3	(1)	Copper chromite (1)	220	1500	4.3	5	0.1	0.1[a]
4	$AlCl_3$ (5)	60% Ni (5) on kieselguhr	175	1000	33	70	2.0	1.0
5	(1)	5% Pd (1) on carbon	30	60	2.0	50	7.2	0.1
6	(1)	5% Pd (0.5) on carbon	40	60	1.5	18	2.2	0.2[a]
7	(1)	5% Pd (0.5) on carbon	50	0	0	0	0	0
8	$AlBr_3$ (0.4)	PtO_2 (0.2)	24	60	1.4	50	1.0	0
9	(1.5)	PtO_2 (0.5)	20	60	2.0	60	3.0	1.0
10	(4.6)	PtO_2 (0.4)	78	60	0.8	25	4.0	0

[a] Traces of diphenyl detected in product.

attempted between Lewis and Brönsted acidity. The possible effect of water in the reagents to form protonic acids was considered beyond the scope of this work.

Hydrogenation of Benzene—High Pressure Rotating Autoclave

The first four experiments included in Table 1 are representative of the preliminary work. Although the results were poor, they clearly demonstrated that the hydroalkylation products could be obtained by this process. We were disappointed, however, that we were unable to duplicate the work of Truffault (*1*) with 60% nickel on kieselguhr, and P_2O_5 (Expt. 1). Since the description of his catalyst is vague—"nickel black"—we decided not to pursue this further.

Only small quantities of phenylcyclohexane and dicyclohexyl were obtained in Expts. 2 and 3 with silica alumina and copper chromite, even at the low hydrogenation rate of Expt. 3. Traces of diphenyl were also found.

The great increase in hydrogenation rate over copper chromite catalyst at 250°C (vs. 220°C) was unexpected. However, the equipment used has large heating surfaces and temperature over-rides often occur. This may explain the high rate. The experiments were included to show that slow hydrogenation rates had little effect on phenylcyclohexane production in this system.

The Hydrogenation of Benzene—Parr Low-Pressure Apparatus

Since phenylcyclohexane is probably the result of consecutive reactions involving a slow hydrogenation step followed by a fast alkylation step, it was decided to continue this study in the Parr low pressure hydrogenation apparatus where a better control of reaction conditions was possible. These studies involved the use of both insoluble and soluble Lewis acid alkylation catalysts and are summarized in the remainder of Table 1 and in Table 2.

An attempt to reduce the hydrogenation rate by reducing the amount of palladium catalyst (Expts. 5 and 6) was successful; however, the amount of phenylcyclohexane was also reduced and traces of diphenyl were also present.

Since diphenyl was found in several of the experiments it was thought that it might be an intermediate to phenylcyclohexane. Kovacic and Kyriakis (*5*) have reported the production of *p*-polyphenyl products using $AlCl_3$–$CuCl_2$ catalysts, a system not completely unlike ours. To investigate this, Expt. 7 was conducted in the absence of hydrogen; no diphenyl could be detected in the product; therefore, it was concluded that diphenyl is not an intermediate for phenylcyclohexane production in our system.

In order to improve the alkylation potential of the system, soluble Lewis acids, $AlBr_3$ and BF_3, were used. Although the results with $AlBr_3$ were not improved (see Expts. 8–10) there was some indication that increasing the catalyst quantity was beneficial.

The BF_3–acetic acid and BF_3–methanol complexes enabled the use of macro quantities of alkylation catalyst compared to hydrogenation catalyst. The results ob-

TABLE 2

THE HYDROGENATION OF BENZENE BATCHWISE AT 100°C WITH $PdCl_2$[a]

Expt. no.	Catalysts (g) Alkylation	Hydrogenation	Solvent	Δ (psig/hr)	Conversion (%) to C_6H_{12}	$C_6H_{11}C_6H_5$	$C_{12}H_{22}$
11	BF_3, (9.3)	$PdCl_2$ (0.2)	Methanol	1.0	41	6.0	0
12	(9.3)	$PdCl_2$ (0.1)	Methanol	1.2	48	1.3	0
13	(7.1)	$PdCl_2$ (0.2)	Methanol	2.1	59	3.7	0
14	(6.8)	$PdCl_2$ (0.2)	Acetic acid	1.3	63	6	0
15	(7.4)	$PdCl_2$ (0.2) + HCl	Acetic acid	1.8	48	6	0

[a] H_2 pressure, 60 psig.

TABLE 3
THE CATALYTIC HYDROGENATION OF TOLUENE[a]

Expt. no.	Catalyst[b]	Poison	Δ (psig/hr)	Conversion (%)		
				MC[c]	TMC[d]	TMC/MC
16	5% Ni on $SiO_2Al_2O_3$	None	1.5	1.6	8.3	5.2
17	"	Pyridine, 30 mg	3.0	6.1	4.5	0.7
18	"	Pyridine, 60 mg	1.8	4.4	0	0
19	"	1.25% As	4.3	5.6	13.3	2.3
20	"	2.5% As	3.9	11.6	6.4	0.5
21	"	5.0% As	2.7	3.8	8.0	2.1
22	60% Ni on kieselguhr	None	17.1	34.5	0	0
23	5% Ni on Al_2O_3	None	1.4	3.9	0	0
24	0.375% Pd on $SiO_2Al_2O_3$	None	5.7	8.7	11.2	1.3
25	0.375% Pt on $SiO_2Al_2O_3$	None	32.3	74.8	1.4	0.02

[a] Sixty psig, 100°C for 6 hr, 5 g of catalyst.

[b] Catalyst ABD, surface area and pore diameter not determined.

[c] Methylcyclohexane.

[d] 1-(*p*-tolyl)- plus 1-(*m*-tolyl)-1-methylcyclohexane.

tained (Table 2) gave at most a 6% conversion of benzene to phenylcyclohexane.

Hydrogenation of Toluene with Supported Metal Catalyst—Parr Low-Pressure Apparatus

A separate study involving the rate of hydrogenation of toluene over various supported metal catalysts was next undertaken. This study was made at low pressure (60 psig) at 100°C and is summarized in Table 3.

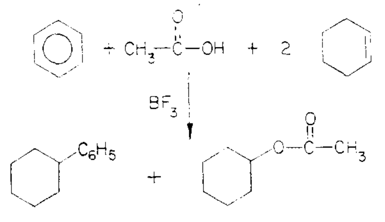
These results clearly show that the hydroalkylation product can be the major product (Expts. 16, 19, 21, and 24) and any effort to control the hydroalkylation process by controlling the hydrogenation rate or alkylation rate via selective poisons [pyridine and arsenic (*6*)] gives inferior results (Expts. 17–21).

Kieselguhr (SiO_2) and Al_2O_3 (Expts. 22 and 23) at 100°C evidently do not have enough acidity to cause any hydroalkylation, and nickel on silica–alumina gave the best result (Expt. 16). Pyridine added to the nickel on silica–alumina almost completely eliminated hydroalkylation (Expts. 17 and 18) and arsenic (Expts. 19–21) improved the hydrogenation activity of the nickel on silica–alumina catalyst and caused a decrease in the conversion to hydroalkylation product. The only clear-cut evidence which supports the belief that reduced hydrogenation rates are beneficial is the comparison of results obtained with nickel, palladium, and platinum on silica–alumina (Expts. 16, 24, and 25). The hydrogenation rates were 1.5, 5.7, and 32.3 Δ psig/hr, respectively, and the hydroalkylation/hydrogenation ratios were 5.2, 1.3, and 0.02.

From these results it is concluded that the inherent hydrogenation activity of the metal and acidity of the surface are the important criteria for hydroalkylation and efforts to try to improve hydroalkylation via selective poisons, temperature, or pressure will not be effective. Pyridine behaved as expected; arsenic did not, for some unknown reason. It might also be anticipated that any catalytic hydrogenation metal less active than nickel on a surface more acidic than silica–alumina, with an aromatic compound more difficult to hydrogenate than toluene, would give a better result than we obtained in our best experiment (Expt. 16).

Mechanism

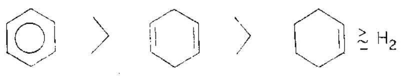
The hydroalkylation product seems to result from an electrophilic cyclohexyl species on the catalyst surface which alkylates the aromatic compound present in abundance. There are, however, questions which arise if a carbonium ion is postulated in the system, since no carbonium ion products were found other than the hydroalkylation product. With benzene, for instance, no methylcyclopentane (*7*) was found, and in the system where BF_3–acetic acid was present, no cyclohexyl acetate (*8*) was formed. To satisfy our curiosity in this respect, we conducted a separate experiment in which cyclohexene was added dropwise at room temperature to a solution of BF_3, benzene, and acetic acid to give a quantitative conversion of cyclohexene to a 1:1 mixture of cyclohexyl acetate and phenylcyclohexane; no methylcyclopentane or cyclohexylhexene was found [Eq. (3)]. This leads to the conclusion that dimerization of cyclohexene, followed by its hydrogenation to form bicyclohexyl, did not occur.



(Eq. 3)

The carbonium ion theory, however, is consistent with the fact that we obtained our best results with toluene (Table 3). Toluene hydrogenation yielded a more stable tertiary carbonium ion, while benzene yielded the more difficultly formed cyclohexyl secondary cation. This is evident since the only hydroalkylation products we got with toluene were the 1-(*p*-tolyl)- and 1-(*m*-tolyl)-1-methylcyclohexane [Eq. (2)], and phenylcyclohexane with benzene. Steric factors probably prevented the *ortho*-isomer formation with toluene.

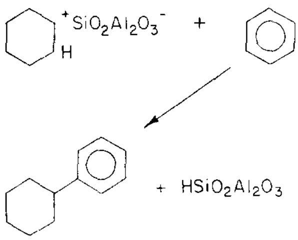
For a better understanding of the results one needs a clearer picture of what is occurring on the catalyst surface. On the metallic sites, hydrogenation is occurring (*9*) and the following species are probably bound to the surface with the following decreasing order of tenacity:



This order would therefore represent a concentration gradient of each component between the metal surface and the bulk phase of the reaction mixture. Smith and Pennekamp (*10*) showed in their work that benzene is more strongly adsorbed onto a catalyst surface than hydrogen by showing that the rate of hydrogenation is affected only by hydrogen pressure. Cyclohexadiene is also strongly adsorbed since we do not find any products relating to its presence, and cyclohexene being less strongly adsorbed, is mobile and reacts with an acid site (*11*) to form a cationic species [Eq. (4)].

(Eq. 4)

This electrophilic species now reacts with the aromatic compound (*12*) whose relative concentration is high [Eq. (5)].



(Eq. 5)

In the BF_3, $AlCl_3$, $AlBr_3$ systems these catalysts form complexes (*13*) with aromatics and the concentration of the complex on the catalyst surface is probably proportional to its solubility or diffusion rate to the catalyst surface. This concentration is probably low since the amount of hydroalkylation obtained was low.

For dual functional catalysts, however, acid sites can be situated adjacent to metal hydrogenation sites so that the diffusion limitation of the process is removed and hydroalkylation becomes the major reaction.

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