(27) Here we attempt only to justify our estimates of the values of K_a, K_{a2}, and K_H, acknowledging that the justification is based on additional assumptions and inexact models; data for β-ketoaldehydes are unavailable. For K_a, we started with $K_a = 2.7 \times 10^{-14}$ *M* for acetaldehyde hydrate and $K_a = 9 \times 10^{-11}$ *M* for chloral hydrate[26] and attempted to estimate the effect of the benzoyl group on K_a for acetaldehyde hydrate by interpolation. The electronic influence of the benzoyl group was estimated from the ionization constants for acetic acid ($K_a = 1.75 \times 10^{-5}$ *M*), trichloroacetic acid ($K_a = 0.219$ *M*), and acetoacetic acid ($K_a = 2.63 \times 10^{-4}$ *M*).[28] The last constant was corrected for substitution of methyl by phenyl, a factor of 1.44 based on $K_a = 2.18 \times 10^{-5}$ *M* for β-phenylpropionic acid and $K_a = 1.5 \times 10^{-5}$ *M* for butyric acid,[29] to give $K_a = 3.78 \times 10^{-4}$ *M* for benzoylacetic acid. For the acids, the factor 1.65×10^{-3} was calculated for the effect of the benzoyl group. $K_a = 1.75 \times 10^{-13}$ *M* for benzoylacetaldehyde hydrate was then calculated by multiplying the factor by (K_a(chloral hydrate) − K_a(acetaldehyde hydrate)) and adding the product to K_a for acetaldehyde hydrate. K_{a2} data, unavailable for aldehydes, are plentiful for dicarboxylic acids and $K_a > K_{a2}$. For *o*-phthalic acid, $\Delta pK_a = 2.46$;[28] for malonic acid, $\Delta pK_a = 2.84$;[28] for *cis*-3,3-diphenylcyclopropane-1,2-dicarboxylic acid, $\Delta pK_a = 6.74$.[30] From these data and the estimated K_a for benzoylacetaldehyde hydrate, $K_{a2} = 10^{-15}$ *M* seems reasonable. For K_H we started with $K_H = 0.7$ for acetaldehyde hydrate and $K_H = 0.03$ for chloroacetaldehyde hydrate[26] and attempted to estimate the effect of the benzoyl group on the value for acetaldehyde hydrate by interpolation. The electronic influence of the benzoyl group was estimated as above using K's for acetic acid and benzoylacetic acid and $K_a = 1.41 \times 10^{-3}$ *M* for chloroacetic acid. For the acids, the factor is 0.26. $K_H = 0.53$ for benzoylacetaldehyde hydrate was then calculated by multiplying the factor by (K_H(acetaldehyde) − K_H(chloral hydrate)) and substracting the product from K_H for acetaldehyde.

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The Strong Acid-Catalyzed Hydrogenation of Aromatics

J. Wristers

Contribution from the Corporate Research Laboratories, Exxon Research and Engineering Company, Linden, New Jersey 07036.

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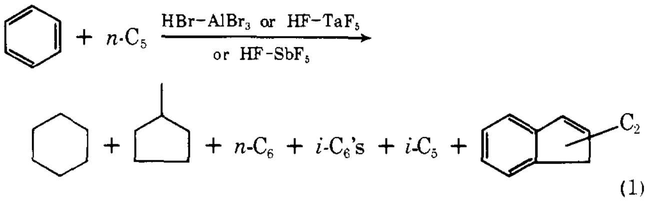
Abstract: The strong acid-catalyzed hydrogenation of benzene has been studied. It is possible to hydrogenate benzene at 50° through protonation with either $HF-TaF_5$, $HF-SbF_5$, or $HBr-AlBr_3$ and reaction of the protonated aromatic with a tertiary hydride source such as isopentane. Ultimately cyclohexane and a number of C_5-alkylated benzenes are formed. No hydrogenation occurs when a secondary hydride source or hydrogen is substituted for the tertiary hydride source. However, when hydrogen is used in conjunction with isopentane, it is consumed. As a result, at pressures greater than 14.6 atm H_2, the reduction becomes catalytic in both acid and isopentane. The function of the hydrogen is to reduce the isopentyl cations formed during the benzene reduction, thereby regenerating the isopentane and a proton. $HCl-AlCl_3$ also catalyzes the hydrogenation of benzene in the presence of a tertiary hydride source, while $HF-TiF_4$, $HF-HfF_4$, and $CF_3SO_3H-TaF_5$ are all inactive.

Superacids offer a novel method to hydrogenate aromatics through protonation and reaction of the resultant carbonium ion with hydrogen. However, attempts to hydrogenate the aromatics benzene[1] and hexamethylbenzene[2] using the acids $HBr-AlBr_3$ and $HF-SbF_5$, respectively, failed. On the other hand, benzene has been hydrogenated in the $HF-TaF_5$-hexane system[3] and in the $HBr-AlBr_3$-3-methylpentane system.[4] In the latter case, the observation was made that no reaction occurred in the absence of the aliphatic solvent.

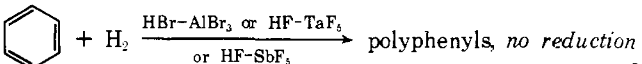
We have investigated the hydrogenation of benzene in all of the above and a number of other superacids and have found that the aliphatic solvent, hydrogen, and the nature of the superacid all play a crucial role in the success of these hydrogenations. This paper presents our results which we will use to rationalize the previous work and to describe the mechanism of the reduction.

Results and Discussion

Aliphatic Solvent. It is possible to hydrogenate benzene in either $HF-TaF_5$, $HBr-AlBr_3$, or $HF-SbF_5$ at 50° in the absence of hydrogen, if an aliphatic solvent capable of donating a tertiary hydride ion is present[5] (eq 1). *n*-Pentane is an excellent solvent because it does not interfere with analysis of products and because it does not undergo the extensive cracking reactions observed for higher molecular weight alkanes. By sampling the hydrocarbon phase of the two-phase systems, one can follow the course of the reaction using gas chromatography. For all of these acids, one observes that the pentane is isomerized to isopentane, and the benzene is reduced to an equilibrium mixture of cyclohexane and methylcyclopentane. When left standing over the acid, these latter products are slowly cleaved to a mixture of isohexanes. There is no evidence for the generation of hydrogen through reaction of the acid with isopentane.[2] After 10-25% of the benzene has been converted to cyclohexane, the reaction stops. Analysis, after quenching with water, indicated that large amounts of C_5-alkylated benzenes had formed in the acid layer. When these reductions were done in the absence of pentane, but in the presence of 35.0 atmospheres of hydrogen, no reduction occurred (eq 2). Clearly molecular hydrogen is not directly involved in this reduction. On the other hand, when both hydrogen and *n*-pentane were present in the HBr-AlBr$_3$ and HF-TaF$_5$ catalyzed reactions,[6] the hydrogenation of benzene proceeded to completion after an induction period during which the pentane isomerized to isopentane (eq 3, Figure 1). This induction period is not observed when an equilibrium mixture of isopentane-*n*-pentane is used (Figure 2). When propane was substituted for pentane in the HF-TaF$_5$ reaction, no reduction of benzene took place (eq 4). These results demonstrate both the necessity of a tertiary hydride source and the absence of any direct hydrogenation by molecular hydrogen in the benzene reduction.



(1)



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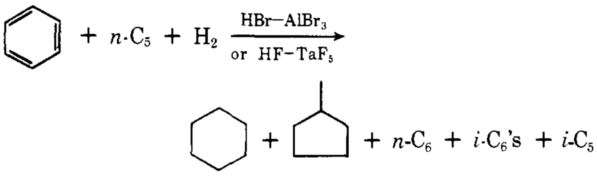

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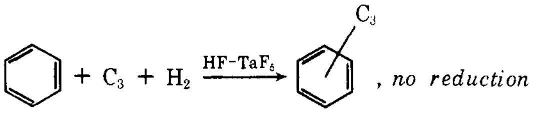
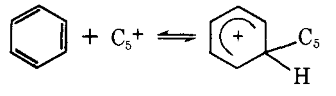


(4)

Hydrogen. While hydrogen does not need to be present in order for some of the benzene to be reduced, it plays an integral role in making the reaction catalytic with respect to acid by preventing alkylations from taking place. In doing so it ultimately supplies the hydrogen for the reduction. It prevents alkylations by reducing the carbonium ions[7] that are formed in the acid, thereby inhibiting the alkylation of benzene (eq 5, 6, and 7).

$$C_5H_{11}^+ + H_2 \rightleftharpoons C_5H_{12} + H^+ \quad (5)$$



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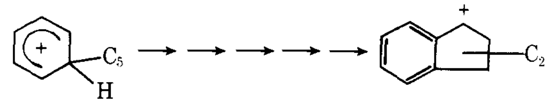

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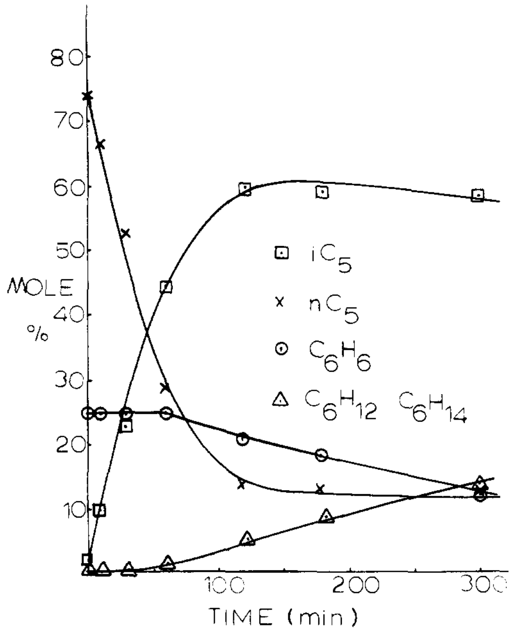


Figure 1. Plot of components of hydrocarbon phase vs. time in the hydrogenation of benzene in the HF-TaF$_5$-*n*-pentane system.

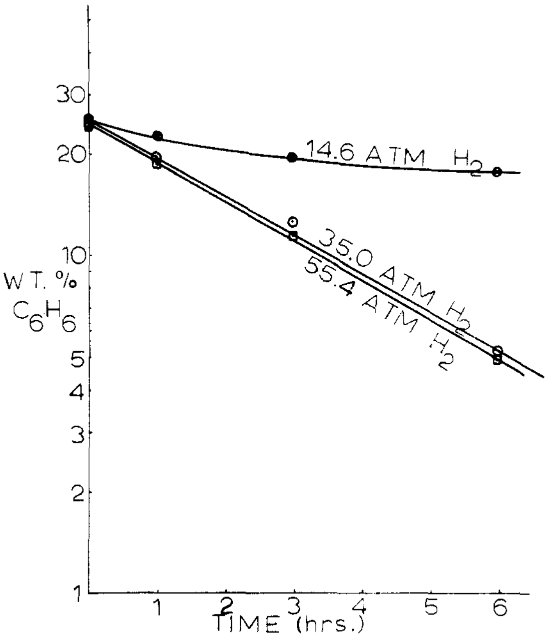


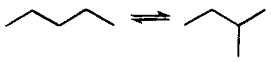
Figure 2. Plot of weight percentage of benzene in hydrocarbon phase (log) vs. time (linear) in the hydrogenation of benzene catalyzed by HF-TaF$_5$-isopentane at different hydrogen pressures.

There is a minimum hydrogen pressure necessary to suppress these alkylations. As the pressure is increased from 0 to 14.6 to 35.0 and to 55.4 atm in the HF-TaF$_5$-pentane catalyzed reaction, there is a concomittant decrease in the formation of alkylated benzenes. Thus, in the reduction involving no hydrogen, 10.0 g of alkylated (predominately C$_5$ alkylated) benzenes formed. This figure decreased to 8.0 g at 14.6 atm, 3.1 g at 35.0 atm and 2.5 g at 55.4 atm. A plot of benzene disappearance vs. time for these reactions (Figure 2) indicates that, at 35.0 and 55.4 atm of hydrogen, the reduction proceeds at a constant rate. Thus, using 0.41 mol of benzene, 0.78 mol of *i*-C$_5$, 0.17 mol of *n*-C$_5$, 2.0 mol of HF, and 0.20 mol of TaF$_5$, the pseudo-first-order rate constant for benzene disappearance is 8.8 × 10^{-5} sec^{-1} at 50°. However, at 14.6 atm, the rate continually decreases and stops after 33% of the benzene is converted. Most of this conversion has been to cyclohexane, but a significant amount has been to alkylaromatic carbonium ions. These carbonium ions are not hydrogenated at these conditions and in tying up the acid reduce the acidity sufficiently to prevent further protonation and thus hydrogenation of the benzene.

Acids. A search was made to see if other superacids would catalyze the hydrogenation of benzene. The search was limited to those acids that were stable both thermally and to reduction by hydrogen. Besides HF-TaF_5, HBr-$AlBr_3$, and HF-SbF_5, hydrogen chloride-aluminum trichloride was also found to catalyze the hydrogenation of benzene. HF-HfF_4, HF-TiF_4, and CF_3SO_3H-TaF_5 were not active. Isobutane was the solvent in the HF-TiF_4 reaction and *n*-pentane in the remainder. The difference in activity of these acids seems to be one of acidity.[8] Both HF-SbF_5[9] and HF-TaF_5[10] are known to substantially protonate benzene. There are no data that any of the inactive acids do. Assuming that there is a relationship between isomerization ability and acidity, we note that all of the active acids easily isomerized the aliphatic solvent that was present, while the inactive ones did so very slowly or not at all.

We conclude from these results that, for an acid to be active, it must be strong enough to substantially protonate benzene. One empirical method to determine the activity of an acid is its isomerization ability.

Mechanism of Benzene Hydrogenation. The results that have been discussed suggest that three essential steps occur during the reduction of benzene in the superacid-pentane-hydrogen system. First a sufficiently strong acid is required to isomerize pentane to isopentane and to protonate benzene (eq 8 and 9). Then the protonated benzene abstracts a hydride ion from isopentane to form a diene and an isopentyl cation (eq 10). The experiments involving the effect of solvent and hydrogen on this reaction establish that not hydrogen or a normal alkane but that a solvent capable of donating a tertiary hydride ion supplies the hydride for this reaction. This fact was also recognized independently by Schneider in the HBr-$AlBr_3$-3-methylpentane system.[4] In support of this Brewer recently reported that the hydride-donating ability of an isoalkane is 10^3 greater than that of a normal alkane.[11] The absence of such a solvent also explains the earlier unsuccessful hydrogenation attempts.[1,2]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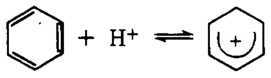

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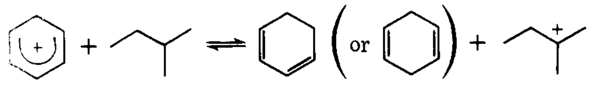

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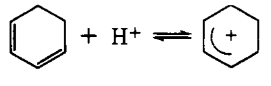

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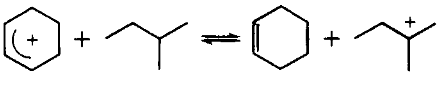

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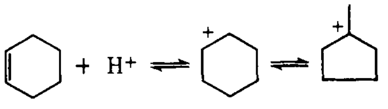
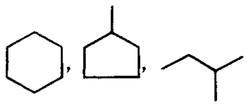
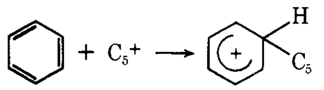


(13)

$$R^+ + H_2 \longrightarrow RH + H^+ \qquad (14)$$

R =


Further protonation and hydride abstractions produce the cyclohexyl cation (eq 11-13). Since it was possible to hydrogenate benzene in pentane in the absence of hydrogen and since hydrogen does not react with allyl cations,[12] isopentane and not hydrogen is the hydride source in these steps. The aliphatic carbonium ions that are formed throughout the reaction react with hydrogen to form cyclohexane, methylcyclopentane, isopentane, and a proton[7] (eq 14), thereby completing the cycle and making the reaction catalytic in both isopentane and acid. In the absence of hydrogen, these carbonium ions alkylate the benzene and then, through deprotonation, hydride transfer, and cyclization, supply the hydrogen necessary for the reduction. This sequence is pictured for the pentyl cation (eq 15, 16, 17, and 18). The number of compounds involved and the exact nature of the steps in this sequence are not known.



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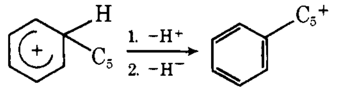

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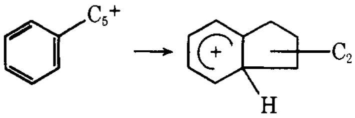

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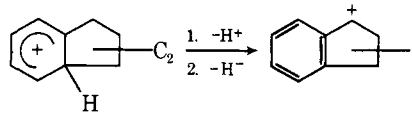

(18)

One question remains unanswered. Why doesn't hydrogen add directly to the protonated benzene instead of adding via the circuitous path involving the aliphatic solvent?[13] We are working to answer this last question and toward extending these reactions to other aromatics and acids.

Experimental Section

Materials. All materials were used without further purification: hydrogen, >99.95%, Linde; benzene, reagent grade, Matheson Coleman and Bell (MCB); isopentane, >99%, MCB; *n*-pentane, >99%, Phillips; hydrogen fluoride, anhydrous, >99.9%, hydrogen chloride, technical, >99.0%, hydrogen bromide, >99.8%, all from Matheson Gas Products; trifluoromethanesulfonic acid, 3M; tantalum pentafluoride, >98%, Ozark Mahoning Co.; aluminum trichloride, >99.77%, Fischer; aluminum tribromide, >99.97, Fischer.

Spectroscopy. Nuclear magnetic resonance spectra were recorded on a Varian A-60 using deuteriochloroform as a solvent and tetramethylsilane as an internal standard.

Gas chromatographic analysis were done on a Varian 2700 series equipped with thermal conductivity detector, dual columns, and linear programmer. Columns and conditions: 10% DC-200 on Chromosorb P, 15 × ⅛ in., programmed from 30 to 175° at 6°/min and 3% Se-30 on 80-100 Chromosorb W, 5 ft × ⅛ in., programmed from 30 to 275° at 10°/min. The DC-200 column separates all hydrocarbons by carbon number from C_2 and C_{10} and all isomers from C_3 through C_6. The Se-30 column detects hydrocarbons up to C_{22}; C_1-C_5 are all analyzed as one, while the carbon content, ±1 carbon, could be established for the range C_6-C_{20}.

Mass spectra were determined on a CEC 21-103 using two programs developed for aromatic analysis of hydrocarbon mixtures. One is run at 11 eV and identifies parent peaks of aromatics containing up to 36 carbons.[15] The other is run at 70 eV and separates hydrocarbon mixtures into paraffins, naphthenes, and different classes of aromatics up to a molecular weight of 225.[16,17]

Benzene, *n*-Pentane, Hydrogen Fluoride, and Tantalum Pentafluoride. This experimental description was essentially followed in all the experiments. Variations are noted in the individual experiments. Benzene (31.6 g, 0.405 mol) 64.8 g (0.898 mol) of *n*-pentane, and 55.2 g (0.200 mol) of tantalum pentafluoride were placed in a 300-ml, stirred, Hasteloy-C autoclave (Autoclave Engineers). The addition was done in an argon atmosphere. Hydrogen fluoride (44.3 g, 2.21 mol) was pressured in using argon to give a total pressure of 7.8 atm at 23°. The mixture was stirred and heated to 50°. Samples were withdrawn from the hydrocarbon phase and analyzed by gas chromatography, DC-200, after 1, 3, and 6 hr of reaction. Analysis of the 1-hr sample, 0.76% ≤ C_4 (butanes and less), 60.81% i-C_5 (isopentane), 12.74% n-C_5 (n-pentane), 0.35% acyclic hexanes, 0.27% MCP (methylcyclopentane), 23.68% C_6H_6 (benzene), 1.35% CyC_6 (cyclohexane), and 0.03% MCH (methylcyclohexane); the 3-hr sample, 1.71% ≤ C_4, 58.00% i-C_5, 12.07% n-C_5, 0.91% acyclic hexanes, 0.63% MCP, 23.34% C_6H_6, 3.10% CyC_6, and 0.23% MCH; the 6-hr sample, 2.65% ≤ C_4, 59.16% i-C_5, 12.27% n-C_5, 1.43% acyclic hexanes, 0.87% MCP, and 0.47% MCH. The total pressure inside the autoclave varied from 8.8 to 9.2 atm during the reaction. After the 6-hr sample, the mixture was cooled and vented into 2000 cm^3 of ice and extracted three times with 300 ml of ether. The combined ether extracts were washed with aqueous sodium bicarbonate, dried with magnesium sulfate, and analyzed by gas chromatography, Se-30 and DC-200. Analysis: 95.78% ether, pentane, and acyclic hexanes; 0.06% MCP, 2.61% C_6H_6, 0.48% CyC_6, and two peaks 0.54 and 0.63% in the C_{10}-C_{11} range. The solvent was removed at reduced pressure to yield 10.0 g of yellow liquid: NMR (five groups of peaks that are assigned to a mixture of C_2-alkylated indenes or isomers thereof) 0.8-1.5 (3-4 H), 1.85-2.1 (4-5 H), 3.0-3.2 (1 H), 5.9-6.1 (0.5 H), 6.9-7.4 (4-5 H); mass spectroscopy (high voltage) 4.21% alkylbenzenes, 84.19% indenes, 9.72% naphthalene;[18] (low voltage) traces of alkylbenzenes, 69.42% C_{11}-indene, and 8.42% C_{12}-indene. The data does not differentiate between a C_2-alkylated indene or its isomer, a C_1-alkylated tetralin that has lost two hydrogens to form an olefin.

Benzene, *n*-Pentane, Hydrogen Bromide, and Aluminum Tribromide. Benzene (15.8 g, 0.202 mol), 64.8 g (0.90 mol) of n-pentane, 86.9 g (1.07 mol) of hydrogen bromide, and 27.0 g (0.101 mol) of aluminum bromide were heated to 70°. Samples that were taken at 0, 1, 3, and 6 hr indicated that the pentane rapidly isomerized to an equilibrium mixture of isopentane-n-pentane, and that the benzene was being converted to cyclohexane and hexanes, e.g., the 6-hr sample, 65.56% isopentane, 15.7.7 n-pentane, 1.71% acyclic hexane, 05% methylcyclopentane, 10.23% benzene, and 2.34% cyclohexane. The pressure inside the autoclave (predominantly HBr) varied between 21.5 and 24.6 atm during the reaction. The final product after a water-ether work-up yielded 7.5 g of red liquid which by GC analysis, Se-30, was found to contain 49.2% ≤ C_6 + ether, 42.2% C_2-alkylated indenes or isomers thereof, and 4.0% C_{10}-C_{18}.

Benzene, *n*-Pentane, Hydrogen Fluoride, and Antimony Pentafluoride. Benzene (31.2 g, 0.399 mol), 64.8 g (0.898 mol) of n-pentane, 44.6 g (2.23 mol) of hydrogen fluoride, and 22 g (0.10 mol) of antimony pentafluoride were pressured to 15.9 atm with argon and heated to 50°. Samples that were taken at 0, 1, 3, and 6 hr indicated that the pentane rapidly isomerized to an equilibrium mixture of isopentane-n-pentane, and that a small amount of the benzene was converted to cyclohexane and acyclic hexanes, e.g., the 6-hr sample, 57.24% isopentane, 12.09% n-pentane, 0.76 acyclic hexanes, 0.41% methylcyclopentane, 26.04% benzene, and 1.95% cyclohexane. No pressure change occurred during the reaction. The final product after a water-ether work-up yielded 5.6 g of a yellow liquid which by GC, Se-30, and NMR analysis was found to contain 19.3% C_6's + ether, 67.2% C_2-alkylated indenes or isomers thereof, and 13.3% C_{16}-C_{18}.

Benzene, Hydrogen, Hydrogen Fluoride, and Tantalum Pentafluoride. To 31.6 g (0.405 mol) of benzene, 43.5 g (2.17 mol) of hydrogen fluoride, and 55.2 g (0.200 mol) of tantalum pentafluoride was added enough hydrogen to give a final pressure of 48.6 atm. The mixture was stirred and heated to 50° at which the total pressure was increased to 55.1 atm using hydrogen. No hydrogen consumption occurred and, after 6 hr, the product was worked up with water-ether to yield, after drying, 496 g of ether extract. GC, DC-200: 98.30% ether, 1.70% benzene, but no cyclohexane or methycyclopentane. The solvent was removed at reduced pressure to yield 8.08 g of a red oil which by GC (Se-30) and NMR analysis was found to contain some ether and benzene and a mixture of di- and triphenyls.

Benzene, Hydrogen, Hydrogen Bromide, and Aluminum Tribromide. To 15.8 g (0.202 mol) of benzene, 86.5 g (1.06 mol) of hydrogen bromide, and 27.0 g (0.101 mol) of aluminum bromide whose combined vapor pressure was 20.0 atm was added hydrogen to give a final pressure of 37.4 atm. The mixture was stirred and heated to 65° at which the total pressure was increased to 55.4 atm using hydrogen. No hydrogen consumption occurred and, after 2.5 hr, the product was worked up with water-pentane-chloroform to yield, after drying, 417.7 g of organic extract. GC, DC-200: 55.4% pentane, 42.16% chloroform, 2.0 benzene, but no cyclohexane or methylcyclopentane. The solvent was removed at reduced pressure to yield 7.9 g of a dark red oil.

Benzene, Hydrogen, Hydrogen Fluoride, and Antimony Pentafluoride. To 31.6 g (0.405 mol) of benzene, 45.0 g (2.25 mol) of hydrogen fluoride, 24 g (0.11 mol) of antimony pentafluoride was added enough hydrogen to give a final pressure of 35.0 atm. The mixture was stirred and heated to 50°. No hydrogen consumption occurred and, after 6 hr, the mixture was cooled and worked up with water and ether to yield 426.7 g of extract after drying. GC, DC-200: 3.41% benzene, traces of some alicyclic hexanes, but no cyclohexane or methylcyclopentane. The solvent was removed at reduced pressure to yield 7.1 g of a viscous red liquid.

Induction Period for Benzene Hydrogenation When Normal Pentane Is Solvent. To 31.6 g (0.405 mol) of benzene, 64.8 g (0.898 mol) of n-pentane, 40-45 g (2.0-2.3 mol) of hydrogen fluoride, and 55.2 g (0.200 mol) of tantalum pentafluoride was added enough hydrogen to give a final pressure of 32.9 atm. The mixture was stirred and heated to 50°. Samples were taken at 0, 10, 30, 60, 120, 180, and 300 min and analyzed by gas chromatography (Figure 1). As hydrogen was consumed it was replenished, thus keeping the total pressure between 32.3 and 37.7 atm. The total hydrogen consumption was 85.4 atm, which corresponds to approximately 0.7 mol of hydrogen.

Benzene, *n*-Pentane, Hydrogen, Hydrogen Bromide, and Aluminum Tribromide. To 7.9 g (0.10 mol) of benzene, 64.8 g (0.898 mol) of n-pentane, 79.1 g (0.978 mol) of hydrogen bromide, 27.0 g (0.101 mol) of aluminum tribromide, whose combined vapor pressure was 18.4 atm, was added enough hydrogen to give a final pressure of 42.7 atm. The mixture was stirred and heated to 70°. Samples taken at 0, 1, 2, and 16 hr indicated that, after the pentane isomerized, the hydrogenation of benzene to cyclohexane commenced, e.g., the 2-hr sample, 0.07 i-C_4, 59.14% i-C_5, 28.56% n-C_5, 0.21% acyclic hexanes, 0.37% MCP, 9.71% benzene, and 1.63% C_yC_6. The 16-hr sample indicated that all of the benzene had been converted and that cracking of the solvent had set in. The total hydrogen consumption was greater than 30.2 atm and corresponds to at least 0.2 mol of hydrogen. The final product, after a water-ether work-up, yielded 5.9 g of brown liquid, which by NMR was analyzed to be a mixture of alkylated aromatics containing <5% olefinic material.

Benzene, Propane, Hydrogen, Hydrogen Fluoride, and Tantalum Pentafluoride. To 31.2 g (0.399 mol) of benzene, 61.5 g (1.40 mol) of propane, 42.6 g of (2.13 mol) of hydrogen fluoride, and 55.2 g (0.200 mol) of tantalum pentafluoride whose combined pressure was 20.1 atm was added enough hydrogen to give a final pressure of 47.9 atm. The mixture was stirred and heated to 50°, and the total hydrogen pressure was increased to 56.6 atm. Samples taken at 1 and 3 hr indicated that there was no conversion of the benzene. There was also no hydrogen consumption. After 4 hr, the reaction mixture was worked up with ice and ether to give 56.1 g of extract. GC, Se-30, of extract: 98.8% ether, 0.61% C_6H_6, and 1.56% C_8-C_{11} (four compounds). Removal of most of the solvent at reduced pressure yielded 2.1 g of a yellow liquid that was analyzed by NMR to be predominantly isopropylbenzene.

Reduction of Benzene under 14.6 Atmospheres of Hydrogen. To 31.6 g (0.405 mol) of benzene, 55.9 g (0.775 mol) of isopentane, 12.5 g (0.173 mol) of n-pentane, 39.3 g (1.97 mol) of hydrogen fluoride, 55.2 g (0.200 mol) of tantalum pentafluoride was added enough hydrogen to bring the total pressure to 11.5 atm. The stirred mixture was heated to 50° at which the pressure was maintained at 14.6 atm by an in-line regulator from a hydrogen source. Samples that were taken at 0, 1, 3, and 6 hr indicated that the benzene was being converted to cyclohexane, methylcyclopentane, and other hexanes (Figure 2). For example, the 6-hr sample, 2.19% ≤ C_4, 59.11% i-C_5, 11.80% n-C_5, 1.92% acyclic hexanes, 1.12% MCP, 17.13% C_6H_6, 6.32% CyC_6, 0.38% MCH. The final product after a water-benzene work-up yielded 8.0 g of a yellow liquid. GC, Se-30: 21.3% C_6H_6, 1.5% C_8, 67.0% C_{10}-C_{12}, 9.2% C_{15}-C_{18}. NMR: benzene, alkylated aromatics, trace of olefins.

Reduction of Benzene under 35.0 Atmospheres of Hydrogen. The previous experiment was repeated with the exception that the pressure was maintained at 35.0 atm at the reaction temperature. Samples that were taken indicated that the benzene was converted at a constant rate to cyclohexane (Figure 2). For example, the 6-hr sample, 3.9 ≤ C_4, 55.46% *i*-C_5, 11.53% *n*-C_5, 13.95% acyclic hexanes, 1.71% MCP, 5.16% C_6H_6, 7.99% CyC_6, and 0.27% MCH. The final product after a water-benzene work-up yielded 3.11 g of a yellow liquid. GC, Se-30: 32.0% C_6H_6, 3.6% C_8, 59.1% C_{10}–C_{12}, traces C_{13}–C_{18}.

Reduction of Benzene under 55.4 Atmospheres of Hydrogen. The previous experiment was repeated with the exception that the pressure was maintained at 55.4 atms at the reaction temperature. Samples that were taken indicated that the benzene was being converted at a constant rate to cyclohexane, methylcyclopentane and acyclic hexanes (Figure 2). For example, the 6-hr sample, 3.67 ≤ C_4, 55.13 *i*-C_5, 11.49 *n*-C_5, 14.87% acyclic hexanes, 1.69% MCP, 4.83% C_6H_6, 8.04% CyC_6, and 0.23% MCH. The final product after a water-benzene work-up weighed 2.5 g (yellow liquid). GC, Se-30: 23.40% C_6H_6, 4.2% C_8, 71.1% C_{10}–C_{12}, traces C_{12}–C_{20}.

Benzene, *n*-Pentane, Hydrogen, Hydrogen Chloride, and Aluminum Trichloride. 3.95 g (0.0505 mol) of benzene, 78.2 g (1.09 mol) of *n*-pentane, 34.4 g (0.943 mol) of hydrogen chloride, and 13.3 g (0.0998 mol) of aluminum trichloride were stirred and heated to 75°, at which the combined vapor pressure was 41.8 atm. Hydrogen was added to give a total pressure of 69.0 atm. Samples that were taken at 1, 2, 18, 25, 42, and 66 hr indicated that the pentane slowly isomerized to isopentane after which the hydrogenation of benzene commenced, e.g., the 25-hr sample, 0.23% ≤ C_4, 65.00% *i*-C_5, 28.83% *n*-C_5, 0.46% acyclic hexanes, 0.31% MCP, 3.87% C_6H_6, and 0.89% CyC_6. After 66 hr, the drop in pressure was 17.6 atm which corresponds to approximately 0.1 mol of hydrogen. The final product after a water-ether work-up yielded 0.47 g of a yellow brown liquid.

Benzene, *n*-Pentane, Hydrogen Fluoride, and Hafnium Tetrafluoride. To 2.24 g (0.0287 mol) of benzene, 56.3 g (0.780 mol) of *n*-pentane, 14.1 g (0.705 mol) of hydrogen fluoride, and 15.3 g (0.0601 mol) of hafnium tetrafluoride was added enough hydrogen to give a final pressure of 21.4 atm. The mixture was stirred and heated to 50°. A sample indicated that no reaction had occurred after 1.5 hr. The reaction was slowly heated to 182° over a 26-hr period. No hydrogen consumption occurred. Samples that were periodically withdrawn indicated that no reaction occurred.

Benzene, *n*-Pentane, Hydrogen, Hydrogen Fluoride, and Titanium Tetrafluoride. To 7.9 g (0.10 mol) of benzene, 61.1 g (1.05 mol) of isobutane, 45.2 g (2.26 mol) of hydrogen fluoride, and 25 g (0.20 mol) of titanium tetrafluoride was added enough hydrogen to give a final pressure of 28.2 atm. The mixture was stirred and heated to 60° at which more hydrogen was added to increase the total pressure from 43.2 to 62.2 atm. A sample indicated that no reaction had occurred after 2.5 hr. The reaction was heated to 90° for 2 hr, sampled, and discarded. This sample indicated 90.66% *i*-C_4, and 9.13% C_6H_6, but no cyclohexane or methylcyclopentane. No hydrogen consumption occurred during the reaction.

Benzene, *n*-Pentane, Hydrogen, Trifluoromethanesulfonic Acid, and Tantalum Pentafluoride. To 3.96 g (0.0507 mol) of benzene, 125 g (1.74 mol) of *n*-pentane, 44.9 g (0.299 mol) of trifluoromethanesulfonic acid, and 26.5 (0.100 mol) of tantalum pentafluoride in a 1000-ml stirred Parr autoclave was added enough hydrogen to give a final pressure of 9.2 atm. The mixture was heated to 50°. Samples that were taken after 1, 14, and 38 hr indicated that some isomerization of the pentane occurred, but that no hydrogenation of the benzene took place. No hydrogen consumption occurred during the reaction.

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References and Notes

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(5) An analogous example of such a reduction has been found in the patent literature in which the reaction of methylnaphthalene with HF–BF_3 and methylcyclopentane produced tetralins and alkylbenzenes along with tar. D. A. McCaulay, U.S. Patent 2,884,469, April 8, 1959.

(6) No further reactions were done with HF–SbF_5 since reduction of the SbF_5 to SbF_3 [J. M. Oelderik, E. L. Mackor, J. C. Platteeniv, and A. van der Weil, U.S. Patent 3,201,494, August 17, 1965; G. H. Olah, J. Shen, and R. Schlosberg, *J. Am. Chem. Soc.*, **92**, 3831 (1970)] or reaction of the benzene with SbF_5 [G. A. Olah, P. Schilling, and I. M. Gross, *J. Am. Chem. Soc.*, **96**, 876 (1974)] destroys the acid.

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(13) It has been suggested that the kinetics of the reaction of hydrogen with a diffuse carbonium ion such as the cyclohexadienyl cation possible via a pentacoordinated transition state[14] would probably be worse than the analogous reaction of hydrogen with a compact positive charge, the isopentyl cation. Thus there is no reaction of hydrogen with protonated benzene, while there is with the isopentyl cation. On the other hand, the abstraction of a hydride from a tertiary carbon may not be so kinetically limited. Personal communication from J. I. Brauman of Stanford University.

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(17) The author thanks Dr. R. Pancirov for help in running and interpreting the mass spectrum programs.

(18) Probably an error in the program. Other methods of analysis did not indicate naphthalene.