

Reactions of Alkylaromatics, Polynuclear Aromatics, and Heteroaromatics in the Strong Acid Hydrogen Fluoride–Tantalum Pentafluoride

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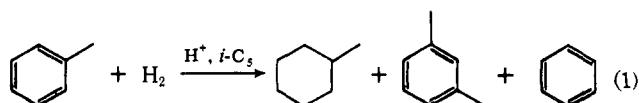
Abstract: The hydrogenation or hydrocracking of representative aromatics using the superacid HF/TaF₅ in conjunction with an isoalkane is described. Alkylaromatics are hydrogenated to cycloalkanes and then may be converted to alkanes. Polynuclear aromatics are partially hydrogenated and then undergo a series of acid-catalyzed dealkylations and hydrogenations to form lower molecular weight aromatics and cycloalkanes or alkanes. Sulfur-containing aromatics are hydrogenated with no other reactions occurring. The mechanism for all these reductions involves initial protonation followed by tertiary hydride abstraction from an aliphatic solvent.

Most of the known chemistry of aromatics in superacids is limited to reactions in which the aromatic framework is preserved or easily regenerated by the reverse reaction, e.g., protonation, alkylation, alkyl group isomerization,¹ sulfonation, radical cation formation,² etc. Because of the use of low temperatures, few reactions have been observed in which the aromatic framework is irreversibly destroyed. At higher temperatures the reactions are much more complex, acids are prone to degradation, and high-pressure equipment that does not react with the acid is required. One interesting example of such a reaction at higher temperatures is the reduction of benzene to cyclohexane. Localized aliphatic carbonium ions are known to react easily with hydrogen.³ However, earlier attempts to reduce benzene⁴ and hexamethylbenzene³ via protonation in the superacids HBr/AlBr₃ and HF/SbF₅, respectively, and reacting the resultant carbonium ion with hydrogen failed. On the other hand, the reduction of benzene has been found to proceed at 50 °C in the HF/TaF₅/hexane⁵ or the HBr/AlBr₃/3-methylpentane systems.⁶ This reduction has been shown to involve transfer of tertiary hydride from the aliphatic solvent to the protonated benzene as the crucial step.⁷ At temperatures of 200 °C benzene is converted to ethylbenzene and tar using the acid HF/TaF₅.⁸ The mechanism of this conversion involves a complex series of protonation, hydride transfer, alkylation, polymerization, and cracking reactions.

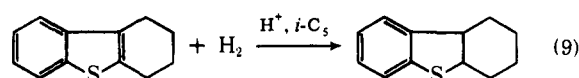
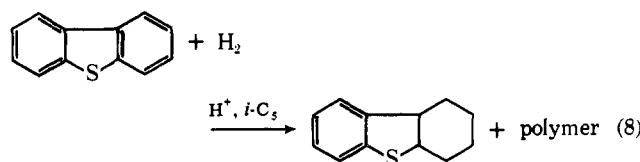
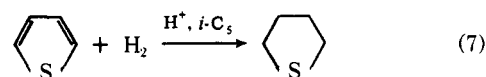
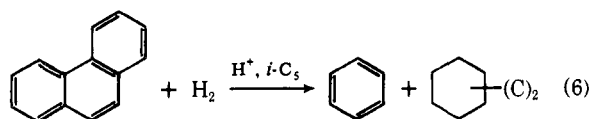
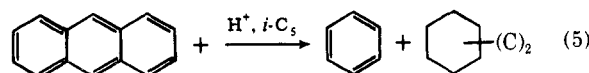
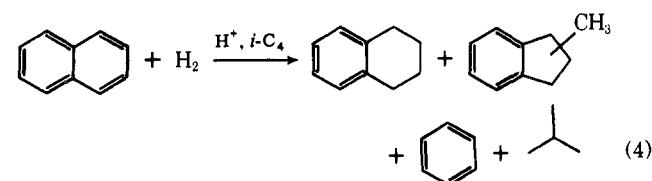
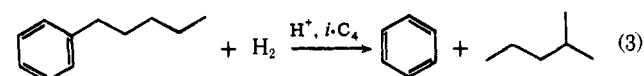
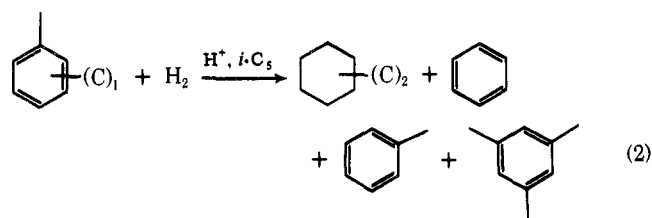
HF/TaF₅ is especially suited for these aromatic conversions as it is an oxidatively and thermally stable, noncorrosive liquid, and sparingly soluble in hydrocarbons. We have studied the conversion of a series of aromatics in this unique superacid at conditions which allow the isolation of the primary products. These results are presented in this paper.

Results and Discussion

The HF/TaF₅ catalyzed conversion of a variety of aromatics has been studied between the temperatures of 50 and 100 °C. All the reactions were carried out in the presence of an aliphatic solvent and hydrogen. The primary products from representative examples are shown in eq 1–9.



The course of all the reactions is followed by continually analyzing the hydrocarbon layer of the three-phase system. Aromatics more basic than toluene are protonated and remain



dissolved in the acid layer. As the aromatics are converted to less basic cycloalkanes and alkanes, they are extracted into the hydrocarbon layer which is easily separated. If the products from the aromatic conversions are left standing over the acid, they are converted further: the aromatics to cycloalkanes, the cycloalkanes to alkanes, and the alkanes to lower molecular

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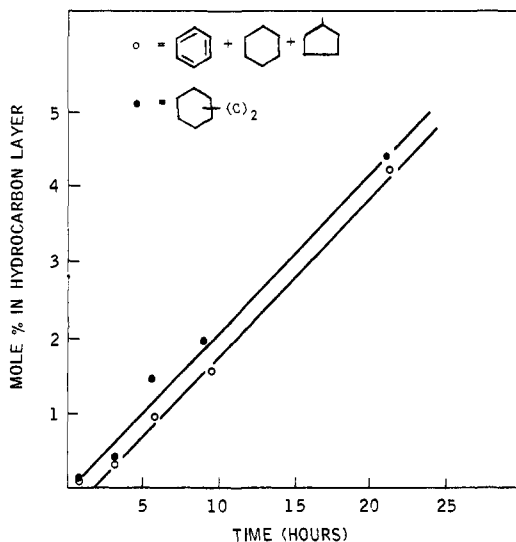


Figure 1. Major products from anthracene conversion vs. time.

weight alkanes. Thus some of the benzene produced in these reactions is always converted to an equilibrium mixture of cyclohexane and methylcyclopentane. The products from the aromatic sulfur compounds are more basic than the starting materials and thus remain protonated in the acid layer. Organics in the acid layer are analyzed by venting the reaction mixtures from each reaction into an ice bath. The mixture is extracted into *n*-pentane, the extract analyzed by GC, and the solvent removed to separate the higher molecular weight products. No alcohols and few olefins are detected by this quenching procedure.

Alkylbenzenes. The conversion of alkylbenzenes may proceed by a number of pathways. Reduction of the aromatic ring ultimately occurs in all cases at stringent enough conditions. However, when the alkyl group is methyl, a significant amount of disproportionation or isomerization to the most stable methylbenzene first takes place¹ (eq 1 and 2). When the alkyl group is larger, e.g., pentyl, dealkylation is the first step (eq 3). The difference in the first step is most likely explained in terms of stability of the carbonium ion generated if dealkylation occurs: dealkylation of methylbenzene would produce an unstable methyl cation, but dealkylation of pentylbenzene produces the more stable isopentyl cation.¹

Naphthalene. The reduction of naphthalene to tetralin takes place quickly at 50 °C. If the tetralin is left standing over the acid, it is slowly hydrogenated to form decalin or dealkylated to form benzene and isobutane (eq 4).

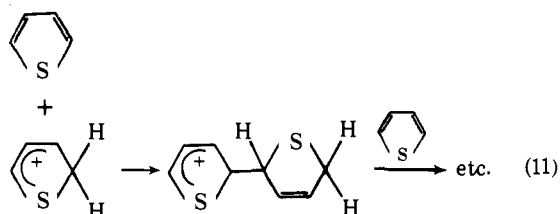
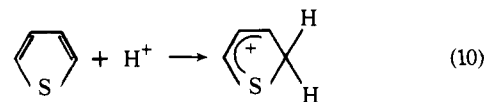
Polynuclear Aromatics. The conversion of the polynuclear aromatics, anthracene and phenanthrene, is more complex. The major products formed in both cases are equal quantities of benzene and dimethylcyclohexanes¹⁰ (eq 5 and 6). This is adequately demonstrated if one plots the mole percentage of these hydrocarbons observed in the hydrocarbon phase vs. time for the anthracene reaction (see Figure 1). Octahydroanthracene intermediates remain in the acid layer until converted to these products. The higher temperatures required for the conversion of these polynuclear aromatics lead to some conversion of the benzene and dimethylcyclohexane products. When the reaction nears completion, hydrocracking of the pentane solvent occurs. This solvent hydrocracking is not surprising because it is known that at temperatures above 50 °C, HF/TaF₅ is an active alkane hydrocracking catalyst.¹¹

We find that the conversion of these basic polynuclear aromatics, and the conversion of the aromatics more basic than toluene, proceed smoothly if the ratio aromatic:tantalum pentafluoride:hydrogen fluoride is kept at 1:2:10. Changes in these ratios by more than 50–100% lead to solvent alkylation

of the aromatic or to solvent hydrocracking. Solvent alkylation occurs in a weak acid, e.g., the ratio of aromatic to TaF₅ is greater than 1. Solvent hydrocracking occurs in a very strong acid, e.g., the ratio of aromatic to TaF₅ is less than 0.25.

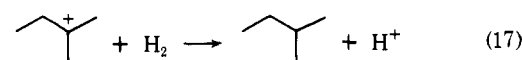
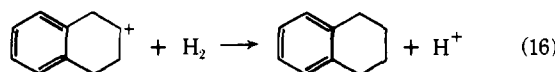
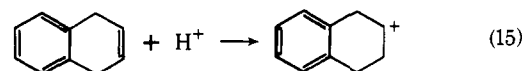
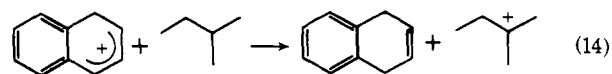
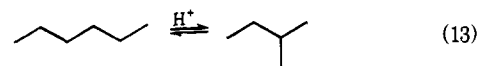
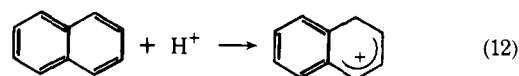
If one is careful to maintain these ratios, then even the reactions of the polynuclear aromatics are found to be catalytic in that 1 mol of acid can convert many moles of the polynuclear aromatic. Thus, we have been able to convert 3 mol of phenanthrene per mol of tantalum pentafluoride over a period of 335 h at temperatures slowly increasing from 50 to 90 °C.

Aromatic Heterocycles. The reduction of thiophene to tetrahydrothiophene occurs readily in the HF/TaF₅/isopentane system. Under similar conditions dibenzothiophene is converted to a mixture of hexahydrodibenzothiophene and a sulfur-containing polymer (eq 8). A small amount of a sulfur-containing polymer is also formed in the case of thiophene when HF is added to a mixture of thiophene, TaF₅, and isopentane. However, when a solution of thiophene in isopentane is slowly added to a mixture of the HF/TaF₅ acid, the polymerization is circumvented. A similar mode of addition cannot be made for dibenzothiophene because of its relative insolubility in isopentane. On the other hand, tetrahydrodibenzothiophene, which is soluble in pentane, is easily hydrogenated to hexahydrodibenzothiophene with no polymer formation using this inverse addition (eq 9). The polymerization observed in these reactions is attributed to the reaction of the protonated heterocycle with the unprotonated heterocycle during the initial stages of HF addition¹² (eq 10 and 11). When a solution



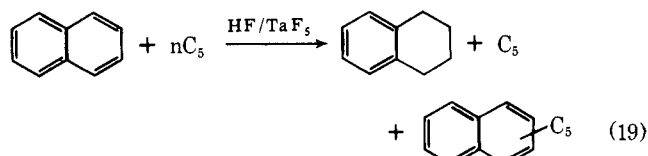
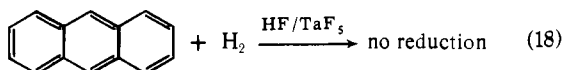
of the heterocycle in isopentane is slowly added to the acid, all of it becomes protonated and only hydrogenation can take place.

Mechanism for Aromatic Conversions. The mechanism for the conversion of these aromatics is analogous to that observed for benzene.⁷ For instance, in the naphthalene conversion, the reaction probably proceeds by the following pathway: the



naphthalene is protonated and then abstracts a tertiary hydride ion from the isopentane to produce dihydronaphthalene and an isopentyl cation (eq 12 and 14). (In all of these reactions when *n*-pentane was used as the solvent, isomerization to isopentane occurs prior to hydrogenation, eq 13.) Protonation of the dihydronaphthalene forms the tetralin cation (eq 15). This cation and the isopentyl cation may react directly with hydrogen to produce tetralin and regenerate isopentane (eq 16 and 17).

Evidence for this hydrogenation mechanism is analogous to that observed for HF/TaF₅/isopentane catalyzed reduction of benzene. (1) These aromatics are not hydrogenated in the absence of an aliphatic tertiary hydride donor (eq 18), (2) but some hydrogenation does take place in the absence of molec-

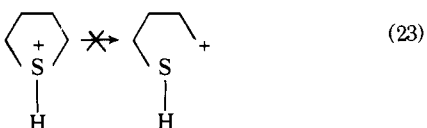
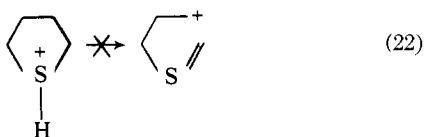
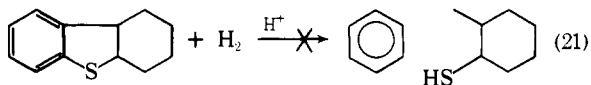
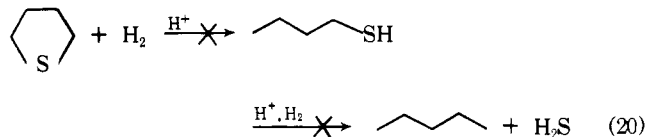


ular hydrogen if such a tertiary hydride donor is present (eq 19). In this last reaction, the *n*-pentane isomerizes to isopentane to produce the tertiary center for hydride ion donation. The hydrogen for the reduction is supplied by alkylation of the naphthalene by the pentane.

Once the tetralin is formed, it will react further if left standing over the acid. A small amount is reduced to form decalin, path 1. The rest is converted to benzene and isobutane by means of a complex series of protonations, isomerizations, and hydrogenations. These reactions are schematically depicted in path 2. The number of compounds and the exact nature of the steps involved in path 2 is not known.

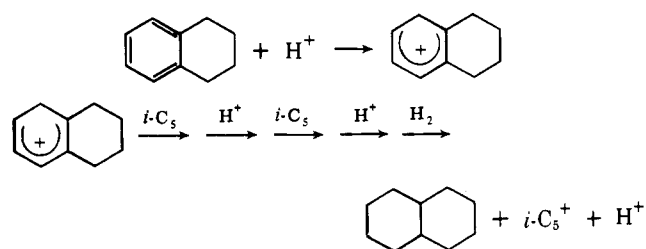
Obviously, the mechanism for the conversion of the alkylaromatics and polynuclear aromatics will involve variations from the mechanism described for naphthalene. However, in each case the mechanism may be divided into analogous acid-catalyzed hydrogenation and cleavage steps.

The mechanism for the conversion of aromatic heterocycles is different from that observed for other aromatics. After reduction of the thiophene to tetrahydrothiophene and of di-

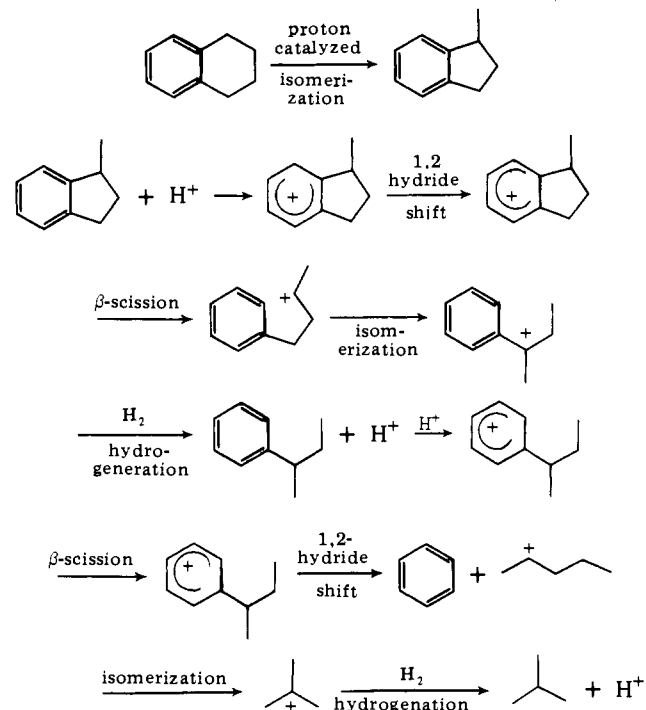


benzothiophene (or tetrahydrodibenzothiophene) to hexahydrodibenzothiophene is complete, the reaction stops. No fur-

Path 1



Path 2



ther acid-catalyzed cleavage of these compounds is observed (eq 20 and 21). The reason for this behavior is that the sulfur in the aromatic starting material is not very basic and protonation at the carbon next to the sulfur is strongly favored.¹³ Reduction in a manner already described for other aromatics then takes place. However, the sulfur in the reduced compound is more basic than any other part of the molecule and is immediately protonated. Cleavage of this protonated compound does not proceed because the product from a β -scission would be very unstable (eq 22). The alternate α -bond cleavage has been shown to be unfavorable because of the unstable primary carbonium ion that would be produced¹⁴ (eq 23).

Experimental Section

Materials. All solvents and reagents were reagent grade unless specified otherwise. Hydrogen fluoride, anhydrous, >99%, was obtained from Matheson Gas Products; tantalum pentafluoride, >98%, was obtained from Ozark Mahoning Co.

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 analyses were done on a Varian 2700 series instrument equipped with thermal conductivity detector, dual columns, and linear programmer. Columns and conditions: 10% DC-200 on Chromosorb P, 15 ft \times 0.125 in., programmed from 30 to 175 $^\circ\text{C}$ at 10 $^\circ\text{C}/\text{min}$. The DC-200 column separates all hydrocarbons by carbon number from C₂ to C₉ and all isomers from C₄ to C₆. The SE-30 column detects hydrocarbons up to C₂₂; C₁-C₅ are all analyzed as one, while the carbon content \pm one carbon could be established for the range C₆-C₂₀. All percentages from GC analysis are area percentages unless otherwise specified.

Table I. Analysis of Hydrocarbon Samples of Anthracene Reaction^a (Area %)

	1 h	6 h	22 h	Benzene extract ^b
≤C ₄	1.16	7.12	14.57	Trace
<i>i</i> -C ₅	74.93	65.90	52.70	Trace
<i>n</i> -C ₅	22.64	16.77	12.96	Trace
<i>i</i> -C ₆ + <i>n</i> -C ₆	1.24	7.78	11.00	Trace
MCP + CyC ₆		Trace	0.79	Trace
C ₆ H ₆	0.05	0.95	3.45	99.03
MeCyC ₆		0.02	0.28	Trace
Me ₂ CyC ₆ + other C ₈ s	0.12	2.11	6.10	0.21
C ₁₀				Trace
C ₁₁ -C ₁₃				Trace
C ₁₄				0.14

^a Abbreviations: ≤C₄ = CH₄ + C₂H₆ + C₃H₈ + C₄H₁₀, *i*-C₅ = isopentane, *n*-C₅ = *n*-pentane, MCP = methylcyclopentane, CyC₆ = cyclohexane, C₆H₆ = benzene, MeCyC₆ = methylcyclohexane, Me₂CyC₆ = dimethylcyclohexane, C₈, C₉, etc., refer to summation of all isomers having that carbon content. ^b Contained a trace (≤0.01%) of toluene and xylene.

Table II. Analysis of Hydrocarbon Phase of Toluene Reaction

	0.5 h	1 h	1.5 h
≤C ₃	0.74	2.29	4.22
C ₄	94.92	94.22	91.45
C ₅	Trace	Trace	0.09
<i>i</i> -C ₆ + <i>n</i> -C ₆	0.37	1.44	3.09
MCP + CyC ₆	0.70	0.57	0.29
C ₆ H ₆	1.72	0.72	0.31
MeCyC ₆	1.05	0.65	0.55
PhCH ₃	0.48	0.07	

Mass spectra were determined on a CEC 21-103 spectrometer 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 alkanes, cycloalkanes, and different classes of aromatics up to a molecular weight of 225.¹⁶

Anthracene, *n*-Pentane, Hydrogen, Hydrogen Fluoride, and Tantalum Pentafluoride. This experimental description was essentially followed in all the experiments. Variations are noted in the individual experiments. Anthracene (17.8 g, 0.100 mol), 64.5 g (0.900 mol) of *n*-pentane, and 55.2 g (0.200 mol) of tantalum pentafluoride were placed in a 300-mL, stirred, Hastelloy-C autoclave. The addition was done in an argon atmosphere. Hydrogen fluoride (41.1 g, 2.05 mol) was pressured in using hydrogen. The mixtures were stirred and heated to 80 °C at which point the pressure was kept at 24 atm by the continual addition of hydrogen. Samples were removed from the hydrocarbon layer and analyzed by GC (DC-200 and SE-30) after 1, 3, 6, 9, and 22 h of reaction. After the 22-h sample, the entire mixture was cooled and vented into 2 kg of ice and extracted with benzene. The benzene extracts were washed with aqueous NaHCO₃ until basic, dried with MgSO₄, filtered, and analyzed by GC. The solvent was removed at reduced pressure to yield 11.9 g of yellow-orange solid, which was analyzed as follows: GC, SE-30, 5.19% decalin, 8.57% C₁₁-C₁₃, traces of partially hydrogenated anthracene, 80.73% anthracene, traces C₁₅-C₁₇; NMR 75% of material is anthracene, the rest looks like a mixture of alkylaromatics; high-voltage mass spectrum (HVMS), 100% aromatic; low-voltage mass spectrum (LVMS), 5.39% benzene (used in extraction) 1.68% tetralin, and 7.15% other indans, 49.23% anthracene, 2.33% dihydroanthracene, 3.09% tetrahydroanthracene, 1.13% hexahydroanthracene, 6.12% octahydroanthracene. See Table I.

Toluene, Isobutane, Hydrogen, Hydrogen Fluoride, and Tantalum Pentafluoride. Toluene (9.2 g, 0.10 mol), 60.5 g (1.04 mol) of isobutane, 45.2 g (2.26 mol) of hydrogen fluoride, and 55.2 g (0.200 mol) of tantalum pentafluoride were pressured with hydrogen, stirred, and heated to 70 °C for 2 h. The total pressure was maintained between 36 and 54 atm using hydrogen. Hydrogen consumption was 0.16 mol

Table III. Analysis of Hydrocarbon Phase of Xylene Reaction

	1 h	23 h	93 h
≤C ₄	0.26	1.85	10.42
<i>i</i> -C ₅	3.26	63.60	66.73
<i>n</i> -C ₅	94.80	32.16	17.75
<i>i</i> -C ₆ + <i>n</i> -C ₆	0.05	0.07	2.57
MCP + CyC ₆		0.18	0.27
C ₆ H ₆	1.05	1.09	0.25
MeCyC ₆	Trace	0.06	0.02
PhCH ₃	Trace	0.31	0.20
Me ₂ CyC ₆ + <i>i</i> -C ₈	0.50	0.20	0.44
Xylenes	0.05	0.06	0.03

Table IV. Analysis of Hydrocarbon Phase of *n*-Pentylbenzene Reaction

	0.5 h	1 h	2 h
≤C ₃	5.08	8.62	9.18
C ₄	78.08	79.06	69.37
C ₅	8.04	9.40	15.83
<i>i</i> -C ₆ + <i>n</i> -C ₆	8.09	9.44	5.39
MCP + CyC ₆	0.40	Trace	Trace?
C ₆ H ₆	0.30	Trace	Trace?
No other compounds			

Table V. Analysis of Hydrocarbon Phase of Naphthalene Reaction

	1 h	3 h	15 h
≤C ₃	0.29	0.19	0.27
C ₄	98.98	98.81	97.70
C ₅	0.45	0.58	0.72
MCP + CyC ₆		Trace	0.35
Benzene	0.28	0.42	0.94
C ₆	Trace	Trace	Trace

± 15%. The reaction progress was followed and the products were analyzed in the manner described for the previous experiment. The yield of heavy products was 1.96 g of a yellow oil which was analyzed by GC and NMR to contain 16% toluene, 71% *m*-xylene, 9% mesitylene, and traces of saturated compounds. See Table II.

Xylene, *n*-Pentane, Hydrogen, Hydrogen Fluoride, and Tantalum Pentafluoride. Xylene (10.6 g, 0.100 mol) (mixture of 20.1% *p*-xylene, 45.8% *m*-xylene, 14.2% *o*-xylene, and 19.9% ethylbenzene), 64.5 g (0.900 mol) of *n*-pentane, 42.0 g (2.10 mol) of hydrogen fluoride, and 55.2 g (0.200 mol) of tantalum pentafluoride were pressured up with hydrogen, stirred, and heated to 80–9 °C for 93 h. The total pressure was maintained between 50 and 55 atm using hydrogen. Hydrogen consumption was 0.26 mol ± 15%. The reaction progress was followed and the products analyzed in the manner described for the previous experiment. The yield of heavy products was 4.23 g of a yellow liquid which was analyzed by GC to contain 15% benzene (used in extraction), 20% *m*-xylene, 33% mesitylene, and 33% tetramethylbenzene (not confirmed). The NMR indicated only methylbenzenes and approximately 10% ethylbenzene. See Table III.

***n*-Pentylbenzene, Isobutane, Hydrogen Fluoride, and Tantalum Pentafluoride.** *n*-Pentylbenzene (14.8 g, 0.100 mol), 58.2 g (1.01 mol) of isobutane, 42.6 g (2.13 mol) of hydrogen fluoride, and 55.2 g (0.200 mol) of tantalum pentafluoride were pressured up with hydrogen, stirred, and heated to 80 °C for 2 h. The total pressure was maintained between 37 and 54 atm using hydrogen. Hydrogen consumption was 0.40 mol ± 15%. The reaction progress was followed and the products were analyzed in the manner described for the previous experiment. The yield of the heavy product was 2.8 g of yellow-brown liquid which was analyzed by GC (SE-30) to be ~20 compounds: 2% C₈, 80% C₁₀-C₁₂, 15% C₁₄. The NMR indicated a trace of olefinic material and the rest appeared to be alkylated aromatics. See Table IV.

Naphthalene, Isobutane, Hydrogen, Hydrogen Fluoride, and Tantalum Pentafluoride. Naphthalene (12.8 g, 0.100 mol), 138.5 g (2.39 mol) of isobutane, 46.5 g (2.33 mol) of hydrogen fluoride, and 55.2 g (0.200 mol) of tantalum pentafluoride were pressured up with hy-

drogen, stirred, and heated to 50 °C for 16 h. The total pressure was maintained between 20 and 23 atm using hydrogen. Hydrogen consumption was approximately 0.2 mol. The reaction progress was followed and the products were analyzed in the manner described for the previous experiment. The yield of the heavy product was 7.10 g of a yellow liquid which was analyzed by a combination of GC and NMR to be 25% benzene (used in the extraction) and 75% tetralin and methylindan.¹⁷ See Table V.

Thiophene, Isopentane, Hydrogen, Hydrogen Fluoride, and Tantalum Pentafluoride. Thiophene (8.4 g, 0.10 mol), 64 g (0.90 mol) of isopentane, 48.5 g (2.43 mol) of hydrogen fluoride, and 55.2 g (0.200 mol) of tantalum pentafluoride were pressured up with hydrogen, stirred, and heated to 80 °C for 5 h in the manner described for the previous experiments. The addition of hydrogen fluoride to the other reagents was done as soon as the other reagents were added. The mixture was stirred rapidly during the addition. (Some polymerization of the thiophene always occurred using this addition method;¹⁸ and if one tarried most of the thiophene polymerized. This polymerization could be circumvented slowly adding the thiophene-isopentane solution to the acid.) The total pressure was maintained between 43 and 53 atm using hydrogen. Hydrogen consumption was 0.20 mol ± 15%. Analysis of the hydrocarbon phase at different times indicated that no sulfur-containing products were present. After 5 h the total reaction mixture was vented into approximately 500 cm³ of ice and extracted with ether. The ether extract was washed with aqueous NaHCO₃ and water, dried with MgSO₄, filtered (this removed the insoluble polymer), and then analyzed by GC (SE-30) to contain only tetrahydrothiophene. The solvent was removed at reduced pressure to yield 4.5 g of a green liquid with a disagreeable odor: GC (SE-30) 2.0% ether, 2.0% C₆, 85.3% tetrahydrothiophene, 9.7% C₈-C₉; NMR predominantly (~80%) tetrahydrothiophene, traces of olefin, possibly some thiophene, and traces of other saturated compounds.

Dibenzothiophene, Isopentane, Hydrogen Fluoride, and Tantalum Pentafluoride. Dibenzothiophene (18.4 g, 0.100 mol), 68 g (0.94 mol) of isopentane, 45.5 g (2.28 mol) of hydrogen fluoride, and 55.2 (0.200 mol) of tantalum pentafluoride were mixed at -78 °C, stirred, and heated to 75 °C for 5.5 h. The total pressure was maintained between 60 and 68 atm using hydrogen. Hydrogen consumption was approximately 0.3 mol ± 20%. The hydrocarbon phase was not analyzed, but in another reaction a small amount, ~0.2%, of benzene was indicated. The heavy product was isolated in the manner described for the previous experiment except that a chloroform/benzene solution was used for the extraction. GC (SE-30) of the extract indicated only two compounds, dibenzothiophene (minor) and a compound that eluted just before dibenzothiophene. The solvent was removed at reduced pressure to yield 12.2 g of a sticky, yellow oil. The products from two such reactions were combined and distilled at 0.2-0.5 mmHg to yield five fractions coming over between 145 and 166 °C, a total of 3 mL, that contained between 60 and 80% of the hexahydrodibenzothiophene. The identity of this compound was confirmed by an independent synthesis.¹⁸ NMR showed a series of multiplets: 1.47 and 1.75 ppm, 8 H; 3.25 ppm, 2 H; 3.80 ppm, 2 H; 7.11 ppm, 4 H. The polymer that was formed in this preparation was separated by combining the total product from two reactions and dissolving in benzene. The benzene solution was then slowly added to a rapidly stirred pentane solution. The yellow precipitate that formed was filtered and dried, yield 15.9 g of yellow powder, 70.33% C, 6.05% H, 15.5% S.¹⁸

Tetrahydrodibenzothiophene, Isopentane, Hydrogen, Hydrogen Fluoride, and Tantalum Pentafluoride. Tetrahydrodibenzothiophene¹⁹ (19.5 g, 0.102 mol) was added to a rapidly stirred mixture of 69.5 g (0.900 mol) of isopentane, 46.5 g (2.38 mol) of hydrogen fluoride, and 55.2 g (0.200 mol) of tantalum pentafluoride kept at 0 °C. The mixture was pressured with hydrogen and heated to 50 °C. The total pressure was maintained between 47 and 68 atm using hydrogen. Hydrogen consumption was 0.13 mol ± 15%. After 21 h the heavy product was isolated in the manner described for the previous experiments: yield 19.1 g of a red liquid; GC (SE-30) 9.5% benzene (used in extraction), 88.9% hexahydrodibenzothiophene, and 1.5% dibenzothiophene. This material was distilled at 110-111 °C (1.5 mmHg) to yield 14.5 g of clear liquid that crystallized at room temperature: GC (SE-30) 96% pure; NMR and GC identical with those of hexahydrodibenzothiophene obtained in the HF/TaF₅-isopentane catalyzed reduction of dibenzothiophene.

Anthracene, Hydrogen, Hydrogen Fluoride, and Tantalum Pentafluoride. Exactly the same procedure, quantities of reagents, and

conditions were used as described for the earlier experiment involving anthracene with the exception that no pentane solvent was present and that the total pressure was maintained at 55 atm using hydrogen. No hydrogen consumption occurred and no light compounds were formed. Yield of the final product was 16.4 g (92% yield) of an orange-yellow solid: GC (SE-30) 100% anthracene; NMR ~95% anthracene; HVMS >99% aromatic; LVMS 62.3% anthracene, traces of partially hydrogenated anthracenes, 6.7% dimer of anthracene.

Naphthalene, *n*-Pentane, Hydrogen Fluoride, and Tantalum Pentafluoride. Naphthalene (12.8 g, 0.100 mol), 157.0 g (2.18 mol) of *n*-pentane, 47.1 g (2.35 mol) of HF, and 55.2 g (0.200 mol) of TaF₅ were stirred at room temperature in the absence of hydrogen. After 20 h the hydrocarbon phase was analyzed by GC: 3.97% C₄, 70.57% *i*-C₅, 20.92% *n*-C₅, 4.37% *i*-C₆ + *n*-C₆, 0.06% C₆H₆. The reaction mixture was worked up in the manner described in the previous experiment: yield 18.2 g of red, viscous liquid; GC (SE-30) 40.59% benzene (used in extraction), 13.03% tetralin + methylindan, 41.44% C₁₃-C₁₆; HVMS 5.63% tetralin + methylindan and a number of C₅-alkylated naphthalenes. The 18.2 g of product was distilled to yield 0.70 g of clear, colorless liquid, bp 115-125 °C (0.03 atm), which was analyzed by a combination of GC and NMR to be a mixture of tetralin and methylindan.

Phenanthrene, Hydrogen, *n*-Pentane, Hydrogen Fluoride, and Tantalum Pentafluoride. Over a period of 335 h 106.8 g (0.600 mol) of phenanthrene dissolved in 2370 g of pentane was added to 47.6 g (2.38 mol) of HF and 55.2 g (0.200 mol) of TaF₅. The mixture was stirred and kept under 41-68 atm H₂. The phenanthrene solution was added in 100-mL batches and then removed prior to adding a fresh batch. A total of 2300 g of hydrocarbon phase was removed in this manner. The temperature was slowly increased from 50 to 85 °C during the reaction time of 335 h. At this time the acid layer was quenched with ice and extracted with CHCl₃ to yield after drying and removal of the CHCl₃ 25.9 g of dark green oil: GC (SE-30) 50.3% C₉-C₁₄ (primarily partially hydrogenated phenanthrene), 49.7% C₁₅-C₁₉; NMR mixture of alkylated aromatics. The 2300 g of hydrocarbon phase was analyzed by GC (SE-30 and DC-200): 0.13% ≤C₃, 0.66% C₄, 60.50% *i*-C₅, 35.34% *n*-C₅, 0.53% *i*-C₆ + *n*-C₆, 0.25% MCP + CyC₆, 1.01% benzene, 1.56% C₈. Most of the solvent was removed from this mixture and the C₈ compounds were separated by preparative GC. They were analyzed by NMR, MS, and C, H analysis to be predominantly a mixture of dimethylcyclohexanes.

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References and Notes

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- (18) The identity of these "polymers" is not known. In some cases they contained small quantities of tantalum. We have not established whether tantalum was an impurity or actually reacted with some of the organic sulfur compound.
- (19) The author wishes to thank Dr. G. H. Singhal of our laboratories for supplying us with a sample of this compound.