

change depending on which and how many compounds were included in the correlation. Acids which fall to the right of the straight-line relationship are compounds whose Me_2SO acidity is comparatively lower. In this group we expect to find compounds AH with relatively large effective radius of A^- . This in fact is the case. For example fluorene, PhCH_2CN , and $(\text{Ph})_2\text{CH}_2$, whose anions have extensive delocalization of the negative charge over large substituent(s), are found in this group. Interestingly all the sulfones fall also to the right of the line. This suggests relatively poor solvation of the corresponding anions. This is probably caused by the large volume of the SO_2 group, which probably carries a significant fraction of the negative charge of A^- .

The nitroalkanes are found to the left of the line in Figure 2. This means that their Me_2SO acidity is relatively higher and suggests specifically favorable solvation of their anions. In the nitroalkane anions most of the negative charge should be located on the protruding (i.e., accessible) and not too large nitro group. This, of course, should lead to relatively good solvation.

Increased alkyl substitution generally leads to a decrease of Me_2SO acidity relative to that in the gas phase. Thus the more highly alkyl substituted carbonyl acids are shifted to the right in Figure 2. This is also true for the sulfones. For example EtSO_2Ph is shifted to the right of MeSO_2Ph in Figure 2. One suspects that the relatively lower acidity in solution is due to charge dispersal and particularly steric hindrance to solvation in A^- caused by alkyl substitution. The relatively lower acidity of the cyclopropyl sulfone in Me_2SO might also be due, at least in part, to steric hindrance to solvation of the partial negative charge located on the carbanion carbon.

In the discussion of the Me_2SO acidities given above, we did not consider effects due to ion pairing. The results of Bordwell et al.⁷⁻¹¹ were obtained at high dilution and these authors believe⁷⁻¹¹ that ion pairing effects were absent. While one can not be certain that ion-pair effects are completely absent,

particularly for ions with charge localized in a small volume (e.g., alkoxide anions), probably they are not serious for the strongly charge delocalized anions of the carbon acids considered in the present work.

Acknowledgment. The financial support of the above work by the Canadian National Research Council is gratefully acknowledged. The measurements of the sulfone gas phase acidities were undertaken with the encouragement of Professor Bordwell whose group also graciously provided most of the sulfone samples.

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Strong Acid Chemistry. 5.¹ Reactions of Cycloalkanes in Hydrogen Fluoride-Tantalum Pentafluoride with Hydrogen

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Abstract: The behavior of several cycloalkanes in the strong acid HF-TaF_5 was investigated at 50 °C and 200 psi of hydrogen. From the results obtained it can be concluded that the reactions proceed catalytically by (1) rapid initial isomerization, where possible, of the cycloalkanes and (2) by a series of selective hydrogenolysis (ring cleavage followed by hydrogenation) reactions to form mixtures of isomeric alkanes. For alkane products with more than six carbon atoms, the end product is the cleavage product. The initial alkane undergoes hydrocracking reactions corresponding to the β -scission products reflecting the stability of alkyl carbenium ions in strong acids, e.g., isobutane > isopentane >> propane from *tert*-butyl, *tert*-amyl, and *sec*-propyl cations, respectively. The rates of hydrogenolysis of the cycloalkanes seems to be a function of both strain energies and the nature of the cations generated.

Among the group of extremely strong acid catalysts, the hydrogen fluoride-antimony pentafluoride and hydrogen fluoride-tantalum pentafluoride systems ($H_0 = \sim -24.33$ and ~ -18.85)² exhibit some unique and important properties. For example, they are also liquid phase hydrogenation catalysts as evidenced by their ability to hydrogenate benzene catalytically.^{3,4} Unlike antimony pentafluoride containing systems,^{5,6} the tantalum pentafluoride system is very stable to reduction

reactions,³ especially by hydrogen⁷⁻¹⁰ and organic ions. We have exploited these unique characteristics in our studies of cycloalkane conversions.

Benzene is converted to cyclohexane in the presence of a noble metal catalyst. In contrast, the methylcyclopentane (MCP) product formed in the acid catalyzed benzene hydrogenation undergoes further reduction via an acid catalyzed hydrogenolysis (ring cleavage and hydrogenation) reaction to

Table I. Rates of Some HF-TaF₅ Catalyzed Cycloalkane Isomerizations^(a)

ISOMERIZATION	T (°C)	k _{iso} × 10 ⁻³ (sec ⁻¹) ^(b)
	40	7.22
	40	5.28
	50	5.00
	50	10.6
	50	4.17

(a) 20 vol % in Freon 113, P_{H₂} = 200 psi, 10/1 (mol/mol) HF-TaF₅.

(b) Rate constants were calculated based on the slope of the concentration (wt %) curve of the isomer charged vs. time (seconds): k_{iso} = (ln C₁/C₂)/(t₂ - t₁).

form an equilibrium mixture of isohexanes. The acid catalyzed ionization and cleavage of cycloalkanes in the HSO₃F-SbF₅ systems have been described by Olah and Lukas¹¹ and by Brouwer and co-workers,^{12,13} respectively. The reaction of alkylcarbenium ions with hydrogen to form saturated hydrocarbons has been reported for benzyl,¹⁴ *tert*-alkyl,¹⁵⁻¹⁷ norbornyl, and methylcyclohexyl.¹⁸ These observations prompted the investigation of the reactions of cycloalkanes that we report here.

The usefulness of the previously described work is limited because of the reactivity of the catalyst with hydrogen. The strong acid system of tantalum pentafluoride in liquid hydrogen fluoride provides a more stable environment to carry out catalytic hydrocarbon hydroconversions hitherto not possible. Most other superacid systems are not compatible with molecular hydrogen and therefore with unsaturated reaction intermediates.

We have found that cycloalkanes undergo very selective acid catalyzed cleavage and hydrogenation reactions in 10:1 (mol/mol) HF-TaF₅ in the presence of hydrogen. The reactions were carried out in stirred Hastelloy C-276 autoclaves using the neat cycloalkane, the cycloalkane diluted in an alkane solvent, e.g., pentane or hexane, and the cycloalkane diluted in Freon 113. The rates of disappearance of the cycloalkanes follow pseudo-first-order kinetics and are also first order in hydrogen partial pressure.

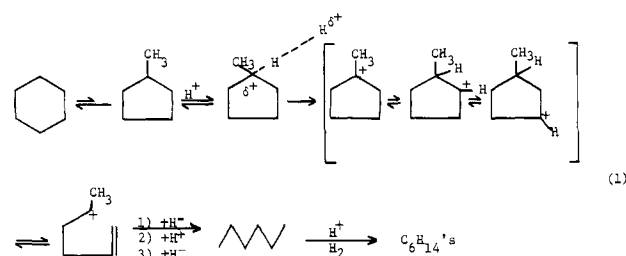
The fact that the hydrogenolysis reactions take place with the neat compound to form the alkane product indicates that the parent cycloalkanes themselves or hydrogen act as hydride ion donors to the initially formed *tert*-alkyl carbenium ions.¹⁹ The NMR spectrum of the acid layer from the reaction of MCP with HF-TaF₅ (discussed below) under 10 psi of hydrogen showed the characteristic multiplet at 2.66-2.76 ppm for an equilibrium mixture of *tert*-hexyl cations. Peaks for MCP⁺ (a very stable cyclic cation) were completely absent. This is in sharp contrast to the observation that the hydrogenation of protonated benzene does not proceed by means of direct reaction with molecular hydrogen.^{3,4}

Cyclohexane (eq 1) rapidly isomerizes at 50 °C and 200 psi of hydrogen partial pressure to its equilibrium composition with methylcyclopentane (MCP) (Table I). We believe that the

Table II. Cleavage of Cycloalkanes in HF-TaF₅

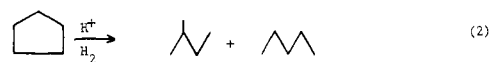
Compound	Strain Energy ⁽²²⁾ (kcal/mole)	Relative Rates of Cleavage at 50°C ^a		
		Neat	20% in R-H	20% in Freon 113
	16.98	-	20	-
	7.28	6	2	4.7
	7.53	1	1	1
	1.94	-	-	3.4
	13.6 ⁽²³⁾	-	-	3.0
	0.87	-	0.1	0.15
	5.7 ⁽²³⁾	-	-	4.5
	2.2 ⁽²³⁾	-	-	-

^aRate constants for MCP hydrogenolysis are (a) neat, 1.11 × 10⁻⁴ sec⁻¹; (b) 20% in *n*-C₅H₁₂, 3.06 × 10⁻⁴ sec⁻¹ and (c) 20% in Freon 113, 5.56 × 10⁻⁴ sec⁻¹. Rate constants are based on the disappearance of the cycloalkane substrate and yields are >90% in all cases.



MCP formed is then ionized to MCP⁺ by direct electrophilic attack of a proton on the tertiary hydrogen, via an S_E1-type mechanism, followed by a β scission of the MCP⁺ and isomerizations to form *tert*-hexyl ions.^{12,13} The presence of hydrogen facilitates the chain-transfer reaction and the facile reduction of the *tert*-hexyl ions to a final product which consists of an equilibrium mixture of isomeric hexanes.




Cyclopentane (CP) (eq 2) undergoes a more rapid hydro-



genolysis (ring cleavage and hydrogenation) than does MCP (Table II) via a secondary cation to form a mixture of isopentanes at 50 °C and 200 psi of hydrogen partial pressure. Since the strain energy (Table II) of CP and MCP are essentially the same, the higher reactivity of the secondary ion is responsible for the faster rate of the cleavage reaction in this case.

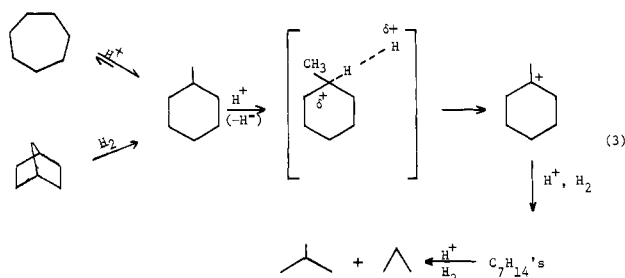
As might be expected, cycloheptane (eq 3), under similar reaction conditions in HF-TaF₅, is rapidly isomerized (Table I) to methylcycloheptane (MCH). The isomerization rearrangement of cycloheptyl cation was reported by Olah and

Table III. Relative Rates of Cycloalkane Hydrogenolysis in Superacids

Compound	Strain Energy ⁽²²⁾ (Kcal/mole)	Relative Rates of Cleavage at 35°C*	
		HF-TaF ₅	HF-SbF ₅
	16.98	25	25
	7.28	1.0	1.0
	0.87	0.1	0.3

*Rate constants for MCP hydrogenolysis in (a) HF-TaF₅, 7.22 × 10⁻⁵ sec⁻¹ and (b) in HF-SbF₅, 3.53 × 10⁻⁴ sec⁻¹.

Lukas¹¹ in an NMR experiment at -60 °C using the HSO₃F-SbF₅ system. At 20 °C they postulated cleavage to heptyl cations but the *tert*-butyl cation was the only identifiable product. We have observed that the methylcyclohexane formed undergoes a relatively slow hydrogenolysis (Table II) via hydride abstraction to form a mixture of isomeric heptanes (eq 3). If the heptanes are permitted to react further, then



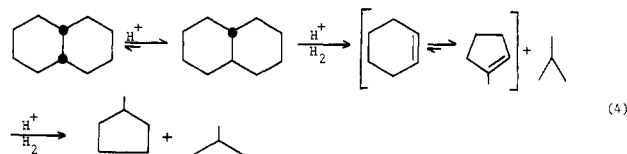
isobutane and propane are the final stable products resulting from heptane hydrocracking reactions.

Norbornane (Nb) (eq 3) undergoes a very rapid and quantitative hydrogenolysis in HF-TaF₅ at 50 °C and 200 psi of hydrogen to methylcyclohexane, the most stable C₇H₁₄ isomer.^{18a,20} A mechanism as postulated by Hogeveen^{18a} involving electrophilic attack of a proton at C-2 or C-7 followed by ring opening and isomerization is most logical (see note 21).

The relative rates of cleavage of MCH vs. MCP vs. Nb fall in the right direction of increasing rate with increasing strain (Table II). Using the more recent strain energy values obtained by Schleyer and co-workers,²² it is seen that the rate of cleavage of norbornane is not quite proportional to strain energy differences: relative rate of cleavage of MCH:MCP:Nb is 1:10:200, while the corresponding relative strain energy ratios are 1:8.6:17. This is seen more clearly (Table III) at lower temperatures where the order of magnitude of the relative reaction rates is essentially the same using both the HF-TaF₅ and the HF-SbF₅ systems. The results suggest that MCP and MCH undergo direct hydride abstraction, whereas Nb, which is more highly strained and which cannot readily form a tertiary cation, is undergoing a much more rapid direct acid catalyzed ring cleavage via an S_E2-type electrophilic attack of a proton at C-2 or C-7. Nb ring opens at a rate which is ~10 times faster than CP, which also must proceed through a secondary cation. Also, since MCP is a better hydride donor than MCH,²⁴ MCP⁺ is a more stable cation than MCH⁺.²⁵ If the hydrogenation of MCP⁺ were the rate-determining step, we would expect that its hydrogenation rate would be slower than that of MCH⁺ and we would observe the reverse order in relative rates.

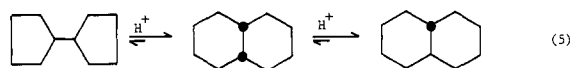
cis-Decalin or a mixture of isomeric decalins undergo rapid isomerization (Table I) in HF-TaF₅ at 50 °C and 200 psi of

hydrogen to the *trans*-decalin isomer which then undergoes a smooth hydrogenolysis reaction to form MCP and isobutane as the primary products (Table II) (eq 4).²⁶ The MCP reacts

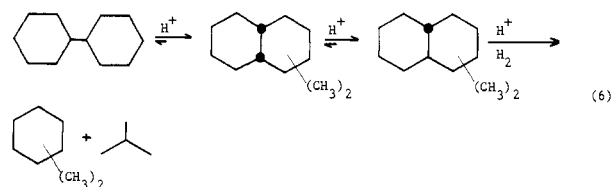


further to form isomeric hexanes as described previously. No dimethylbicyclo[3.3.0]octane or bicyclo[3.2.1]octane was observed as has been reported by reaction of decalin with aluminum bromide, aluminum chloride, or hydrogen iodide at temperatures of 100, 130, and 300 °C, respectively.^{27,28} Zelinsky and Turowa-Pollack²⁹ also found that, when aluminum chloride was reacted with decalin, the low boiling products were cyclohexane, methylcyclohexane, and trimethylcyclohexane which they postulated were formed as a result of degradation followed by resynthesis. Such products might be expected from 4-9 bridge cleavage of a methylbicyclo[4.3.0]nonane (see below) under more severe reaction conditions than were used in our studies. In the MCP vs. decalin case, the order of reactivity of the two tertiary ions is opposite to what strain energy considerations alone would predict.

Bicyclopentyl does not undergo direct hydrogenolysis, but rather preferentially isomerizes very rapidly to *cis*-decalin (eq 5)³⁰ which isomerizes and can be isolated or reacted as in eq 4.



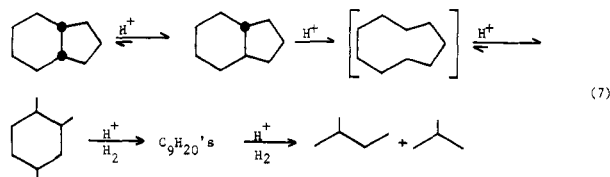
Analogously bicyclohexyl isomerizes directly to *cis*-dimethyldecalin(s) (Table I) which then isomerize to the *trans* isomer(s) which also can be isolated or reacted further to form dimethylcyclohexane(s) and isobutane as the initial reaction products (Table II) (eq 6). This is in contrast to Olah's ob-



servation that bicyclohexyl in HSO₃F-SbF₅ at room temperature loses a tertiary hydrogen to form an ion which undergoes a rapid 1,2-hydride shift.¹¹ The dimethylcyclohexane(s) are converted to isomeric octanes and, if allowed to go to completion, the final product of the C₈H₁₆ cycloalkane hydrogenolysis reaction is essentially all isobutane.

cis-Hydrindane was observed by Zelinski and Turowa-Pollack²⁹ to be isomerized into the *trans* isomer by aluminum bromide. We have observed a similar isomerization of *cis*- to *trans*-bicyclo[4.3.0]nonane followed by a rapid cleavage across the 4-9 bridge, probably to cyclononane (not observed) which rapidly isomerizes to the much more stable 1,2,4-trimethylcyclohexane isomer. Such a cleavage pathway, as opposed to the decalin cases, can be attributed to the large strain energies for *cis*- and *trans*-bicyclo[4.3.0]nonanes of 9.86 and 8.76 kcal/mol, respectively.²² The trimethylcyclohexane reacts much more slowly with hydrogen to form isomeric nonanes which in turn hydrocrack to form isobutane and isopentanes as the stable end products (eq 7).

The final alkane products observed in the above reactions can easily be rationalized on the basis of known carbenium ion stabilities in acidic media.³¹



Summary

The selective acid catalyzed isomerization and hydrogenolysis reactions of several cycloalkanes have been studied in HF-TaF₅ in the presence of hydrogen. The reaction mechanisms which involve hydrogenation of intermediate carbocations do not differ in this acid vs. SbF₅ containing strong acid systems. The nonreducible HF-TaF₅ strong acid system provides a much more stable environment in which to carry out these reactions catalytically. The observed rates of cleavage of the cycloalkanes depend upon both the nature of the intermediate cation which is generated, e.g., secondary > tertiary, and its strain energy. The initial products are isomerized alkanes and, where the initial product has more than six carbon atoms, it undergoes further reaction to form alkane products which reflect the known stability of alkyl carbenium ions in strong acids.

Experimental Section

Cycloalkanes used were commercial chemicals of the highest available purity (usually >99%) and purity was doubly checked by GC analysis.

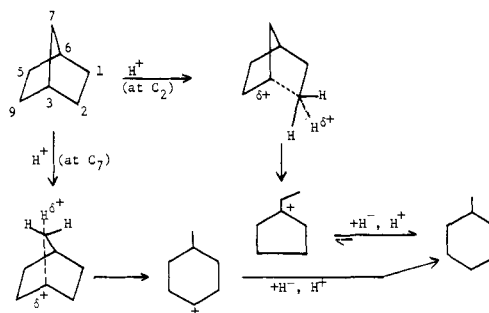
Reaction of Cycloalkanes in HF-TaF₅. The following procedure was followed. Into a 400-cm³ Hastelloy C-276 Autoclave Engineer's magnadrive stirred autoclave was placed tantalum pentafluoride (83.0 g, 0.30 mol) under a stream of nitrogen. The reactor was closed and hydrogen fluoride (60 g, 3 mol), which was distilled at 19.6–20.5 °C from a copper still, was transferred from a 150-cm³ 316 stainless steel cylinder by direct connection to the reactor and pressured by hydrogen into the reactor. The catalyst mixture was stirred under 200 psi of hydrogen at 1000 rpm using a gas sparging flat bladed turbine and heated to 50 °C. Upon reaching 50 °C the pressure was vented to ~100 psig and either (a) 150 mL of the pure cycloalkane, (b) 30 mL of the cycloalkane diluted in 120 mL of *n*-pentane or *n*-hexane, or (c) 30 mL of the cycloalkane diluted in 120 mL of Freon 113 (1,1,2-trichlorotrifluoroethane from Matheson Gas Products) was pressured by hydrogen from a tared 300-cm³ 315 stainless steel cylinder until the reaction pressure was 250 psig. After ~10 s of stirring at 50 °C, a liquid sample was taken for zero time kinetic analysis. This was accomplished by connecting an evacuated 10-cm³ stainless steel cylinder cooled to and maintained at -78 °C (Dry Ice-acetone) to the reactor. Hydrogen was then purged through the sampling dip leg of the reactor to assure a homogeneous sample not diluted by unreacted material. The tubing between the valves was then evacuated and the valves connecting the two vessels were opened and the hydrocarbon sample was passed from the reactor through the dip stick into a 2-cm³ lock-hopper zone in which it was isolated and then pressured into the evacuated 10-cm³ sampling cylinder by the difference in pressure. After the valve to the reactor was closed, 40 psi of nitrogen was pressured through the lock hopper into the sampling cylinder to ensure complete sample transfer. The sample cylinder at -78 °C was vented and a 0.1-μL aliquot was analyzed on a Perkin-Elmer Model 900 gas chromatograph with a flame ionization detector using a 300-ft DC550 capillary column at 35 psig programmed from -20 to +175 °C at a

2.5°/min. Similarly, liquid samples were taken for analysis periodically, i.e., after 3, 5, 7, 10, 20, and 30 min of reaction.

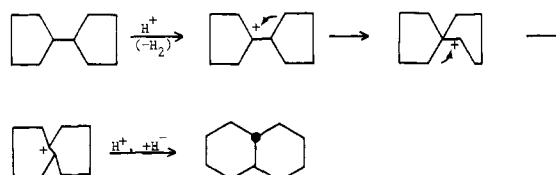
Acknowledgment. The author acknowledges helpful discussions with Dr. Richard H. Schlosberg.

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