dro-7,8-dimethoxy-2-methylisoquinoline (**44**, 53 mg) as a caramel, whose spectral data were identical with those of the racemate. Further elution with benzene–methanol (99:1 v/v) gave a solid, which was recrystallized from ethanol to afford (+)-9,10-dimethoxy-2,3-methylenedioxyochotensane (**43**, 33 mg) as colorless crystals: mp 104–105 °C (lit.[5] 104–105 °C); $[\alpha]^{18}_{D}$ +54° (lit.[5] $[\alpha]^{16}_{D}$ +60°); CD (MeOH) nm ($\Delta\epsilon$) 294 (+1.70), 277 (−0.75), 210 (+44.12), 200 (−41.91).

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Registry No.—**1a**, 62860-05-3; **1b**, 62815-47-8; **2a**, 62815-48-9; **2b**, 62815-13-2; **3a**, 58116-07-7; **3b**, 62815-49-0; 4, 62860-06-4; **8**, 62815-50-3; **9**, 60354-88-3; **10a**, 62815-51-4; **10b**, 62815-52-5; **11**, 62860-07-5; **12a**, 62815-53-6; **12a** HCl, 62815-54-7; **12b**, 62815-55-8; **13a**, 62815-56-9; **13b**, 62815-57-0; **14a**, 62815-58-1; **14a** HCl, 62815-59-2; **14b**, 62815-60-5; **15**, 62815-61-6; **15** HCl, 62815-62-7; **16**, 62815-64-9; **17**, 62815-65-0; **18**, 62860-08-6; **19**, 62815-33-2; **20**, 62815-34-3; **21**, 62815-35-4; **22**, 62815-36-5; **23**, 62815-37-6; **24**, 18028-11-0; **25**, 62815-38-7; **26**, 62815-39-8; **27**, 62815-40-1; **28**, 62815-41-2; **29** HCl, 60356-10-7; **30**, 62815-42-3; **31**, 62815-43-4; **32**, 62815-44-5; **39**, 62860-02-0; **40**, 56974-42-6; 41, 62815-45-6; **42**, 62860-03-1; **43**, 56974-43-7; **44**, 62815-46-7; (±)-[13,13,14-$^2H_3$]xylopinine, 62860-04-2; propionic anhydride, 123-62-6; propionaldehyde, 123-38-6; (*R*)-(+)-canadine, 2086-96-6; sodium bis(2-methoxyethoxy)aluminum hydride, 21608-56-0.

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Heterogeneous Catalysis by Solid Superacids. 2.[1] Reduction of 2-Chloropropane and Its Reaction with Alkanes over Niobium Pentafluoride on Graphite

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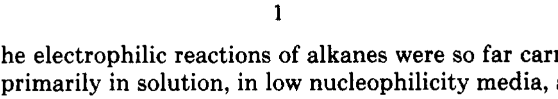
Niobium pentafluoride on graphite was found to be an effective catalyst for the reduction of 2-chloropropane and its reaction with alkanes. In the absence of alkanes, 2-chloropropane is reduced to propane. Reaction of 2-chloropropane with C_3–C_5 alkanes having secondary or tertiary carbon atoms occurs readily accompanied by reduction. The major reaction is Bartlett–Nenitzescu type hydrogen transfer between the generated isopropyl cation and the corresponding alkane. Alkylation products are also formed, but in lower yield. Pentane and 2-methylbutane give in addition substantial amounts of 2-methylpropane. Methane, ethane, and 2,2-dimethylpropane were found to be unreactive under the reaction conditions.

Electrophilic reactions at carbon–carbon and carbon–hydrogen single bonds by strong electrophiles have been well established in recent years.[3] Alkanes, being weak σ bases, are not easily attacked and relatively strong electrophiles are needed. Protolytic reactions of alkanes by superacids,[4–7] nitration by nitronium salts,[8] halogenation by "positive" halogens[9–11] (such as formed by the reaction of elementary halogen with silver salts), as well as alkylation by carbenium ions[12–14] were reported. The mechanism of these reactions involves front side attack of the electrophile on the corresponding σ bonds to form a two-electron three-center bonded carbonium ion (**1**), which then cleaves to give the substitution product and an ionic product, i.e., proton or carbenium ion (eq 1).



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The electrophilic reactions of alkanes were so far carried out primarily in solution, in low nucleophilicity media, and were catalyzed by superacid catalysts (usually based on SbF_5 or TaF_5). Prolonged reaction time and continuous contact with the catalyst can, however, cause extensive secondary reactions of the products. In contrast to electrophilic aromatic substitutions where products are generally stable (for example, nitrobenzenes, halobenzenes, or alkyl benzenes), this is not the case in electrophilic aliphatic substitution. For example, it is possible for R_1E (eq 1) to react further under the

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acidic reaction conditions. Tertiary nitro or halo compounds are extremely sensitive to acids, as are, to a somewhat lesser extent, secondary compounds. Branched alkanes are also prone to react under highly acidic conditions. Other possibilities are secondary reactions of R_2^+ (eq 1), like alkylation, fragmentation, or rearrangement.

The use of solid acid catalysts offers a convenient way to remove the products from further interaction with the catalyst. Conducting the reactions in a flow system enables controlling the contact time and separating the products easily without quenching the reaction mixtures.

Continuing our studies of solid superacid-catalyzed reactions we studied the reaction of 2-chloropropane (**2**) with alkanes in the gas phase over a catalyst comprised of niobium pentafluoride on graphite.

Experimental Section

Reactor. The reactions were carried out in a vertical glass tube reactor with a fixed bed catalyst. The catalyst was held in place by a glass wool plug and the reactants were passed through the catalyst bed. Gaseous reactants were introduced via flow controllers and liquids via syringe pumps. After initial mixing the reactants passed through a 70-cm glass tube heated to 70 °C to ensure complete evaporation and mixing. The catalyst was kept at 45 °C. Samples were taken at regular intervals with a gas syringe via a rubber septum and were analyzed by gas chromatography.

Experimental Procedure. Finely ground NbF_5 (10 g) (Ozark-Mahoning Co.) and 25 g of graphite (−20 + 65 mesh) were mixed thoroughly and heated in a slow stream of dry N_2 to 80 °C for 2 h. Intercalated NbF_5 was prepared by heating NbF_5 with graphite to 120 °C for 48 h under N_2 atmosphere. The catalyst thus prepared was charged into the reactor in N_2 atmosphere. The reactor was heated to 45 °C and the alkane introduced, replacing N_2, at the rate of 2 mmol/min. Samples were taken at time intervals and analyzed. Analysis showed only the presence of the unchanged alkane. 2-Chloropropane (**2**) was then added at the rate of 1.6 mmol/min to the feed. Under these conditions the average contact time of the feed with the catalyst was about 16 s. Fresh catalyst was used for each experiment in order to standardize conditions. In one experiment **2** was passed through the reactor at the rate of 1.6 mmol/min at 45 °C for 5 h. The used catalyst (12 g) was washed with ether to remove organic material and NbF_5,[15] leaving 7.8 g of graphite. The ether solution was washed with water and dried, and the ether evaporated. Oily polymer (1.1 g) was obtained. The material balance in NbF_5 was in good agreement with the initial composition of the catalyst. The weight of the polymer corresponds to 9% of the weight of **2** passed through the catalyst. ^1H NMR of the polymer shows a broad singlet at 0.9 ppm (~50% of the area), a broad triplet at 1.7 ppm (ca. 30%), and two small broad singlets at 2.1 and 2.6 ppm (15 and 5% of the area, respectively). Elementary analysis: C, 83.16; H, 11.01; Cl, 2.48; F, 0.07.

Analysis. Products were analyzed by gas chromatography on a squalane capillary column (150 ft × 0.01 in.) at 70 °C. This column separates well alkyl halides and C_5 and higher alkanes. C_1 to C_4 alkanes were separated on an alumina column (3 m × 1/8 in.) at 150 °C. Peak integrations were carried out with an Infotronics CRS-100 electronic integrator and the results were corrected for differences in the detector sensitivity.

Results and Discussion

The Catalyst. In the present study of the reaction of 2-chloropropane (**2**) with alkanes under heterogeneous gas-phase conditions, NbF_5 on graphite was used as catalyst. Niobium pentafluoride is known to be a Friedel–Crafts catalyst, but few details of its catalytic activity were given.[16] In recent years catalysts prepared from NbF_5 and strong protic acids, such as FSO_3H or CF_3SO_3H as well as HF, were found to be good catalysts in electrophilic reactions of alkanes[17] and aromatic compounds.[18]

The role of graphite in the catalyst is mostly that of a support. Solid, neat NbF_5 was also found to be an effective catalyst. For comparison we carried out the reaction between **2** and 2-methylbutane over NbF_5 on graphite, as well as over neat NbF_5. NbF_5 on graphite gave somewhat better yields and higher conversion. Adsorption of the reactants to graphite may seem to promote the reaction, but this effect is not very significant. The presence of graphite, however, reduces significantly the amount of polymer formed. In the absence of graphite, polymer formation is increased ca. ten times. Minimizing side reactions by the presence of graphite also affects the lifetime of the catalyst as the polymer blocks the active sites and reduces the activity. The dilution of NbF_5 by graphite, i.e., reduction of the concentration of the active sites, helps to decrease polymer formation.

Table I. Volatile Products of the Reaction of Neat 2 over NbF_5

	Onstream time, min			
Product composition, %	20	70	150	270
C_3H_8	39.0	25.0	8.5	1.7
i-C_4H_{10}	1.5	1.0	0.9	0.2
i-C_5H_{12}	0.2	0.2	0.1	Tr
i-PrCl	59.3	73.8	90.5	98.1

We have also prepared the intercalation compound of 20% NbF_5 in graphite. Lately, there is increased interest in the intercalation compounds of metal fluorides,[19] and their catalytic activity in Friedel–Crafts reaction was reported.[20] However, reactions over graphite intercalated NbF_5 showed low conversions and the reactivity of the catalyst was rather quickly reduced. In the graphite intercalated compound most of the NbF_5 is deposited between the lattice layers and thus is not readily accessible to the reactants. Only a small fraction of NbF_5 exposed at the surface edges is catalytically active, where the gaseous reactants can reach the catalyst. This may explain the lower activity of intercalated NbF_5, but a definite answer to this problem cannot yet be given.[21]

Reaction of Neat 2 in the Absence of Alkane. When neat **2** was passed over the catalyst copious evolution of HCl was observed. The mixture of gases was analyzed after different onstream times. The results are given in Table I. The major product is the corresponding parent alkane, i.e., propane, resulting from reduction of **2**. The yield of propane decreases with onstream time due to accumulation of polymer on the catalyst (vide infra). By simple graphic extrapolation the initial composition of products is 50% **2**, 48% propane, 2% 2-methylpropane, and 0.2% 2-methylbutane.

When **2** is passed over NbF_5 it is assumed to ionize via the equation

$$\underset{\mathbf{2}}{(CH_3)_2CHCl} + NbF_5 \rightarrow \underset{\mathbf{3}}{(CH_3)_2C^+H\ NbF_5Cl^-} \qquad (2)$$

to the isopropyl cation **3** or to form a highly polarized donor–acceptor complex (like the methyl fluoride–SbF_5 complex[12,22]), although with the reactive secondary system ionization seems probable. Several reaction paths are open to **3** to explain the results: chloride abstraction to regenerate **2** and NbF_5; proton elimination to form propene; and hydrogen abstraction to give propane.

Chloride abstraction producing **2** and NbF_5 cannot be distinguished from an incomplete reaction. The collapse of **3** to its starting materials, however, seems highly probable. It should be mentioned that abstraction of fluoride ion to give 2-fluoropropane and $NbClF_4$ is far less probable. Such a process is thermodynamically unfavorable. In addition 2-fluoropropane was not found as a product.

Proton elimination from **3** would form propene with HCl evolved and NbF_5 regenerated. Formally it is an E1 elimination reaction of **2**. Propene, however, has never been found in the gaseous products, not even in trace amounts. Being a much better nucleophile than alkanes, propene is readily attacked by **3**, thus initiating a cationic polymerization process. The polymerized products are nonvolatile and stay in the reactor. Only viscous liquids are obtained under the reaction conditions, which do not favor high molecular weight products as the polymer chains are also cleaved by the acid catalyst. The amount of polymer formed in a typical experiment was 9% of **2** fed into the reactor. The strong methyl absorption at δ 0.9, in the ^{1}H NMR spectrum, indicates extensive branching of the polymer. Similar spectrum was obtained when butane was polymerized with SbF_5–FSO_3H.[23] Incorporation of Cl into the polymer, as found by elemental analysis, shows that chloride abstraction takes place in the termination step of the polymerization. On the other hand, the practical absence of fluorine incorporation indicates that there is neither chlorine–fluorine exchange nor quenching by fluoride ion to any significant degree.

Hydride abstraction by **3** with its reduction to propane has only two precedents. Formation of saturated hydrocarbons and HCl from 2-chloro-2-methylbutane and "anhydrous" $AlCl_3$ was first observed by Friedel and Crafts a century ago.[24] Such reactions were not further mentioned in the vast literature dealing with Friedel–Crafts chemistry. Only recently have Siskin and Schlosberg[25] reported that alkyl halides, including **2**, react with several strongly acidic media (HCl–$AlCl_3$, HBr–$AlBr_3$, HF–TaF_5), in the absence of added alkane, to give the parent alkane as a major product. This observation was not limited to secondary or tertiary halides because ethyl chloride and even methyl chloride were found to react to give the corresponding alkanes, i.e., ethane and methane in HF–TaF_5 solution.

The source of hydrogen required for the reduction of **2** to propane is not clear. The absence of any significant amount of protic acid in our system excludes the possibility of reduction by the catalyst. The source of the hydrogen must be a second molecule of **2**.[26] One possibility is that **3** hydride-abstracts from a second molecule of **2**.

$$\underset{\mathbf{3}}{(CH_3)_2C^+H} + \underset{\mathbf{2}}{(CH_3)_2CHCl} \rightarrow (CH_3)_2CH_2 + \underset{\mathbf{4}}{(CH_3)_2C^+Cl} \qquad (3)$$

4 was found to be a stable carbocation under stable ion conditions[27] as were other α-halo carbenium ions.[28] **4** can subsequently proton-eliminate to give 2-chloropropene, which then can participate in the polymerization process. This may be another source for the chlorine incorporation into the polymer. Another possibility is hydride abstraction from propene by **2**, forming propane and allyl cation. The formation of diisopropylchloronium ion can also be involved

$$(CH_3)_2C^+H + ClCH(CH_3)_2 \rightleftharpoons [(CH_3)_2CH]_2Cl^+ \rightleftharpoons (CH_3)_2CHCl + HC^+(CH_3)_2 \qquad (4)$$

but in the secondary system the latter is not expected to effect the reduction.

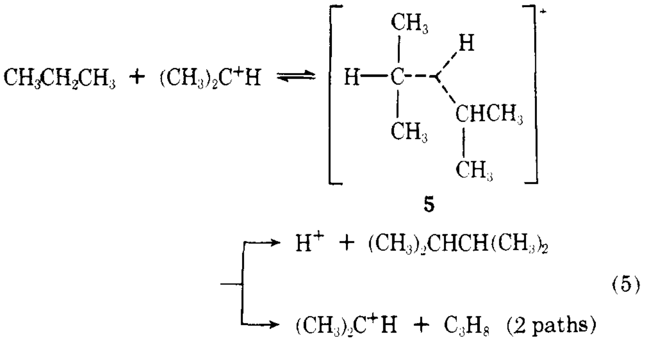
Attempted Reaction of 2 with Methane, Ethane, and 2,2-Dimethylpropane. **2** was reacted with three alkanes which contain only primary carbon–hydrogen bonds, i.e., methane, ethane, and 2,2-dimethylpropane. The ratio of **2** to the alkane was 1:1.25. In all cases the product hydrocarbon mixture obtained was strikingly similar. After 30 min onstream time the alkane composition was ~15% propane, ~1% 2-methylpropane, ~0.2% 2-methylbutane, and ~84% of the starting alkane. The yield of propane decreased with onstream time. For example, only 6.5% of propane was formed after 3 h. There is polymer formation in the reactor, which decreases the effectiveness of the catalyst.

Taking into account the independence of the product composition from the reactant alkane and the similarity to the products obtained from neat **2** (in all cases the hydrocarbon product composition is ~95% propane, ~4% 2-methylpropane, and ~1% 2-methylbutane) we are led to the conclusion that methane, butane, and 2,2-dimethylpropane do not react under the reaction conditions with **2** and we observe only the reduction of the latter.

Reaction of 2 with Propane. Reaction of **2** with propane gave, besides the starting materials, 0.5% of 2-methylpropane, 0.3% of 2-methylbutane, and 0.9% of 2,3-dimethylbutane. HCl was also evolved.

Nenitzescu and Dragan[29a] as well as Bartlett, Condon, and Schneider[29b] found that alkyl halides are reduced to the parent alkane when treated with isoalkane (containing tertiary hydrogen) in the presence of anhydrous aluminum halides. The carbenium ion formed abstracts hydrogen from the isoalkane to give the parent alkane and another carbenium ion. Further reaction of the newly formed ion then takes place. Such a hydrogen exchange is possible in our system too. But Bartlett–Nenitzescu hydrogen transfer between **3** formed from ionization of **2** and propane is a degenerate process. Hydrogen exchange was observed to occur between **3** and propane *in* SbF_5–SO_2ClF *solution* at −78 °C by NMR spectroscopy,[13] and the same process is expected to take place in the present system.

The reaction mechanism is shown in eq 5. The most convincing evidence for electrophilic attack on the secondary C–H bond of propane by **3** is the formation of the corresponding C_6 alkylation product, 2,3-dimethylbutane. Proton elimination from the carbonium ion intermediate **5** gives 2,3-dimethylbutane as product. Alternative cleavage of the three-center bond in **5** will re-form the starting materials according to the degenerate hydrogen transfer.



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(5)

Reaction of 2 with Butanes. In the reaction of **2** with butanes the symmetry of pentacoordinated carbonium ion intermediate is removed and hydrogen exchange is no more a degenerate process. A higher degree of hydrogen exchange is expected in the case of 2-methylpropane due to its more active tertiary C–H bond. Typical product distributions of the reactions are given in Table II.

The amount of propane decreases with prolonged onstream time, but is fairly constant during the first 3 h. Again, polymer formation on the catalyst decreases its efficiency.

In the reaction of **2** with butane the composition of alkyl halides obtained were: 70% unreacted **2**, 23% of 2-chloro-2-methylpropane, and 7% of 2-chlorobutane. With 2-methylpropane 63% of **2** and 37% of 2-chloro-2-methylpropane were obtained. The relative yields of the alkylation products (C_6–C_8) are given in Table III. In both reactions the major reaction product is propane. This further strengthens the argument of a similar hydrogen transfer reaction with propane and **2** which, in this case, is degenerate and thus cannot be observed without labeling experiments. The 2-butyl cation which is formed in the hydrogen transfer of butane with **3** either gives 2-chlorobutane or rearranges to the *tert*-butyl cation and then gives 2-chloro-2-methylpropane. It must be noted that the amount of alkyl chlorides detected is always smaller than expected according to the stoichiometry of the interchange reactions. The most probable reason is that proton elimination from the intermediate alkyl cations (**3** and

Table II. Volatile Products of the Reaction of 2 with Butanes

	Reactant	
Alkane products	Butane	2-Methylpropane
Propane	28	38
Butane	70	
2-Methylpropane	1.5	60
C_6–C_8 alkanes	0.5	2

Table III. Relative Amounts of C_6–C_8 Alkanes Formed in Experiments Shown in Table II

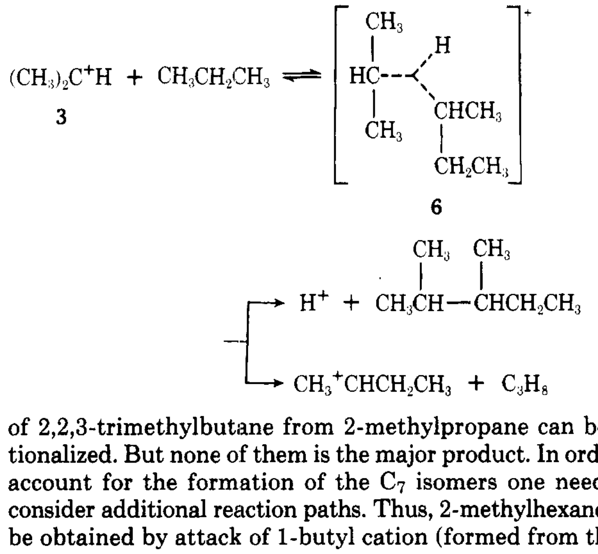
	Reactant	
Product	Butane	2-Methylpropane
2,3-Dimethylbutane	63	65
2,4-Dimethylpentane	18	14
2,2,3-Trimethylbutane	1.5	4
2-Methylhexane	7	7
2,3-Dimethylpentane	7	5
3-Methylhexane	1	5
Octanes	2.5	

2-butyl cation) gives alkenes which subsequently polymerize, competing with quenching by chloride anion. The relative amount of the butyl halides and **2** fits well the proportions of propane and butane. The ratio [propane]/[*n*-butane] is equal to the ratio ([*s*-BuCl] + [*t*-BuCl])/[*i*-PrCl] (in accordance with the assumption that the rate of proton elimination from both secondary cations is similar and that elimination from the more stable *tert*-butyl cation is less important).

The reaction of the alkanes is far from being complete. Only 28% of *n*-butane and 38% of 2-methylpropane reacted. The rather short contact time of the reactants with the catalyst in the flow system explains the relatively low yields, but at the same time side reactions are minimized.

Concerning alkylation products, some 2,3-dimethylbutane is always formed in the reactions. It indicates the reaction between **3** and propane formed in the reaction. Two isomeric octanes are formed when *n*-butane is the reactant formed via the alkylation of butane by the 2-butyl cation. Their absence in the reaction with isobutane hints to the relative lack of the reactivity of the *tert*-butyl cation toward alkanes.

Formation of heptanes, i.e., $C_3^+ + C_4$ alkylation products such as 2,3-dimethylpentane, from the reaction of *n*-butane is easily explained by proton elimination from the intermediate carbonium ion **6** (eq 6). In a similar way the formation



(6)

of 2,2,3-trimethylbutane from 2-methylpropane can be rationalized. But none of them is the major product. In order to account for the formation of the C_7 isomers one needs to consider additional reaction paths. Thus, 2-methylhexane can be obtained by attack of 1-butyl cation (formed from the 2-butyl cation by 1,2 H shift) on propane. 2,4-Dimethylpentane is formed by the attack of isobutyl cation (formed from the 2-butyl cation by 1,2 CH_3 shift) on propane. 3-Methylhexane is formed by the attack of the 1-propyl cation on *n*-butane.

Acid-catalyzed isomerization of the heptanes is a better explanation for the observed isomeric products than the direct independent alkylation processes. Indeed, the similarity of the C_7 fraction regardless which butane was used suggests ready interconversion of the isomeric heptanes. Once a C_7 alkane is formed it can ionize to a tertiary heptyl cation. This cation rapidly equilibrates with other tertiary heptyl cations and then hydrogen transfers to give the hydrocarbon. All heptanes present can ionize to give tertiary cations. 3-Ethylpentane was not detected in the products, but it was previously shown[30] that the related tertiary ion, viz. triethylcarbenium ion, is present in superacidic solution only at very low temperatures and rearranges readily to other, more stable, tertiary heptyl cations. All other isomeric heptanes absent from the products, i.e., *n*-heptane, 2,2-dimethylpentane, and 3,3-dimethylpentane, would be derived from energetically less favorable secondary or primary cations. The absence of the latter two alkanes from the products shows that the stability of the alkane itself is not a determining factor because these neutral alkanes have a low free energy of formation among the isomeric heptanes.[31]

Equilibration of heptyl cations in solution was observed both in FSO_3H–SbF_5[32] and in HF–SbF_5.[33] There is only a qualitative agreement between these ion compositions and our present results. As these were obtained in a heterogeneous system at a significantly higher temperature, such differences in composition are not unexpected.

The rate of rearrangement of heptyl cations is not yet known. Kinetic study of the rearrangement of tertiary hexyl cations in solution was reported.[33,34] The data show that the slower rearrangements (those involving a change in branching) have a rate constant of the order of $0.05\ s^{-1}$ at 0 °C. From activation energies a half-life of $\sim$0.1 s is estimated at 45 °C. Reactions which do not involve change in branching are appreciably faster. If similar rates of isomerization of heptanes are to be accepted under the present experimental conditions, there is sufficient time for equilibrium with the contact times of the present study.

Isomerization of *n*-heptane on several solid acid catalysts in the gas phase[35] showed the C_7 fraction to contain, apart from unrearranged starting material, the same products as observed in the present work. 2,2-Dimethylpentane, 3,3-dimethylpentane, and 3-ethylpentane were absent.

The reaction of **2** with butanes or that of butyl cations with propane in solution at −78 °C[13] showed that the heptane isomer distribution is dependent upon the starting materials. At the low reaction temperature there is relatively little isomerization of the intermediate cations. Upon hydrogen transfer still all isomeric heptanes were obtained, indicating significant amounts of 2,2-dimethylpentane, 3,3-dimethylpentane, and 3-ethylpentane.

Reaction of 2 with Pentanes. The products of the reaction of **2** with pentane and 2-methylbutane are given in Table IV. As already mentioned, 2,2-dimethylpropane does not react under these conditions.

As seen from the data 2-methylpropane is formed in substantial amounts. Once a C_8 carbonium ion is formed by the electrophilic attack of **3** on pentane it will readily rearrange and cleave to the *tert*-butyl cation and 2-methylpropane, both being very stable species.[31,36] This cleavage can be schematically shown by

$$C_3^+ + C_5 \rightarrow [C_8^+] \rightarrow [C'_8{}^+] \rightarrow (CH_3)_3C^+ + (CH_3)_3CH \qquad (7)$$

The *tert*-butyl cation will then either proton eliminate and polymerize or be quenched by chloride to give 2-chloro-2-

Table IV. Reaction of 2 with Pentanes—Volatile Products

	Reactant	
Products	Pentane	2-Methylbutane
Propane	20	27
2-Methylpropane	4	30.5
2-Methylbutane	20	36
Pentane	49	
2,3-Dimethylbutane	2	2
3-Methylpentane		0.5
2-Chloropropane	3	2
2-Chloro-2-methylpropane	2	2

methylpropane. The amount of 2-methylpropane formed from pentane is smaller, probably because of incomplete reaction with 2 (pentane has no tertiary C–H bonds) or because of insufficient branching of the C_8 cation intermediate.

In order to substantiate this suggested reaction path we also reacted 2 and the highly branched 2,2,4-trimethylpentane in the presence of NbF_5 at room temperature, in the liquid phase (the reaction mixture is heterogeneous). Product analysis showed that additional isomeric octanes, all of them highly branched, form in small amounts. The main product is 2-methylpropane (from the fragmentation of the octyl cations according to eq 7).

Similar behavior is known in homogeneous superacid solution chemistry. Whereas C_7 cations are stable and do not cleave, but only rearrange, at −20 °C,[33] C_8 cations must be prepared at −100 °C and they begin to cleave to *tert*-butyl cations at −75 °C.[32] The great stabilities of the *tert*-butyl cation and 2-methylpropane make the cleavage energetically favorable.

Registry No.—**2,** 75-29-6; **3,** 62882-91-1; NbF_5, 7783-68-8; butane, 106-97-8; 2-methylpropane, 75-28-5; pentane, 109-66-0; 2-methylbutane, 78-78-4; methane, 74-82-8; ethane, 74-84-0; 2,2-dimethylpropane, 463-82-1; propane, 74-98-6.

References and Notes

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