solution of **13** from **5** was inhibited by 2,3-iminosqualene; however, the hydration reaction of **5** to the *vic*-glycol was not inhibited, indicating that this is not enzymically produced at the same site as the sterol **13**.

The racemic bisnor analog **6** was transformed rapidly in >95% yield by solutions of oxidosqualene-sterol cyclase[17] or microsomal suspensions to the corresponding *vic*-glycol; little, if any, sterol was produced. Analog **7** also yielded little, if any, sterol; some glycol (*ca.* 10% conversion)[17] was formed in this case, but the rate of hydration of **7** was distinctly slower than that for **5** or **6**.

Of special interest in the above results are (1) the formation of lanosterol analogs from **4** and **5**, and the much more efficient conversion with the former, (2) the formation of *vic*-glycols by catalyzed hydration of the oxides **5–7**,[18] and especially the lack of stereospecificity and efficiency of conversion with **6**, and (3) the greater measure of cyclization with **5** using microsomal rather than soluble enzyme preparations.

Additional study of these and related analog systems is planned. One interesting possibility is that there may be a nonspecific, "detoxifying" or scavenging enzyme in liver microsomes which catalyzes hydration of oxirane derivatives, especially if the ring is not highly substituted (*cf.* ref 10).

Acknowledgment. We are grateful to Bruce Ganem, Dennis Crouse, and Paul Ortiz de Montellano for valuable experimental assistance and to the National Science Foundation and National Institutes of Health for financial support.

[18] The oxides **4–7** were found to be completely stable in 0.1 *M* phosphate buffer at pH 7.4 under incubation conditions. Boiled enzyme solutions at pH 7.4 were without effect on **4**, **5**, **6**, and **7**.

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Chemistry in Super Acids. I. Hydrogen Exchange and Polycondensation of Methane and Alkanes in FSO_3H–SbF_5 ("Magic Acid") Solution. Protonation of Alkanes and the Intermediacy of CH_5^+ and Related Hydrocarbon Ions. The High Chemical Reactivity of "Paraffins" in Ionic Solution Reactions[1]

Sir:

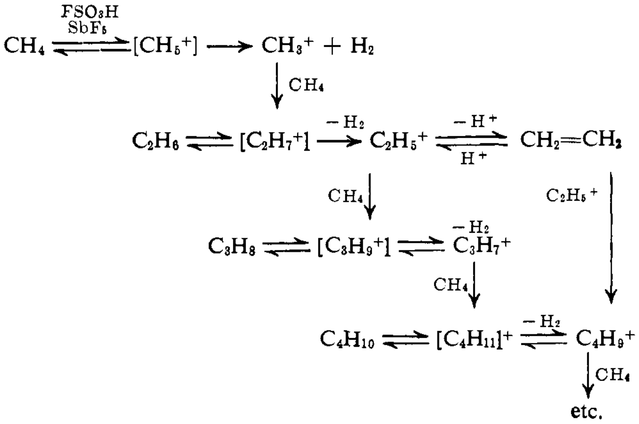
In previous studies[2] we reported that the extremely strong acid FSO_3H–SbF_5 ("magic acid") is capable of forming alkylcarbonium ions from alkanes *via* hydride (alkide) ion abstraction. It was observed that even neopentane is basic enough to undergo reaction in the neat acid. At room temperature, neopentane gave the *t*-butyl cation and methane, and, when reacted at low temperatures in acid diluted with SO_2ClF, the dimethylethylcarbonium ion is formed through the rearrangement of the intermediate neopentyl cation. Hogeveen and Bickel[3] subsequently made similar observations on the protolytic cleavage of neopentane in the related acid system, HF–SbF_5.

We reported[2] that "Methane reacts only at +140° with FSO_3H–SbF_5 to give, as yet, unidentified products. Ethane gives a mixture of 90% $(CH_3)_3C^+$ and 10% $(CH_3)_2C^+CH(CH_3)_2$ through some dimerization and trimerization pathways."

We wish now to report our studies relating to the behavior of methane, as well as ethane, neopentane, and related saturated hydrocarbons, in super acid solution.

Methane, when allowed to react either in a pressure bomb with tenfold excess of 1:1 FSO_3H–SbF_5 solution or at 140° under atmospheric pressure, gives primarily the trimethylcarbonium ion with some higher molecular weight hydrocarbon ions also formed. If the temperature is kept around +80°, a mixture of the trimethylcarbonium ion and the dimethylisopropylcarbonium ion is formed. Depending on the temperature, reaction time, and acid concentration, higher molecular weight hydrocarbon ions can also be formed in various amounts. Hydrogen gas is liberated in the reactions but, as reported previously,[2] it at least partially reduces the acid if not swept ont continuously and therefore the reaction cannot be monitored by measuring the amount of hydrogen formed. When methane was allowed to react with FSO_3D–SbF_5 (prepared also from DF–SbF_5 with SO_3) or CD_4 (obtained from Merck Sharp and Dohme of Canada) with FSO_3H–SbF_5, recovered "unreacted" methane showed extensive hydrogen scrambling as analyzed by mass spectroscopy. HD was also detected in the mass spectroscopic analysis of the gaseous reaction mixture, along with higher molecular weight ion products. All these observations can be explained only by suggesting that, in the super acid solutions, methane indeed is behaving as a base. It is protonated in solution to the CH_5^+ ion which then either undergoes reversible deprotonation accounting for the hydrogen exchange or loses hydrogen to form the extremely reactive carbonium ion $(CH_3)^+$ which then reacts with excess methane to start a "growth reaction" or "polycondensation" giving, eventually, the trimethylcarbonium ion, dimethylisopropylcarbonium ion, or higher molecular weight hydrocarbon ions (Scheme I). The over-all process is, of course, more complicated as the intermediate ethyl cation, isopropyl cation, and related carbonium ions themselves can undergo various di-, tri-, and polymerization processes, and the higher molecular weight hydrocarbon ions undergo, in turn, fragmentation. The hydrogen-exchange reaction of methane seems to be much faster than the polycondensation and can be observed even

Scheme I



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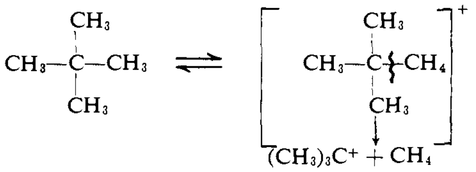
[1] Presented in part at an Organic Colloquim, Harvard University, Cambridge, Mass., Nov 28, 1967.

[2] G. A. Olah and J. Lukas, *J. Amer. Chem. Soc.*, 89, 2227, 4743 (1967).

[3] H. Hogeveen and A. F. Bickel, *Chem. Commun.*, 635 (1967).

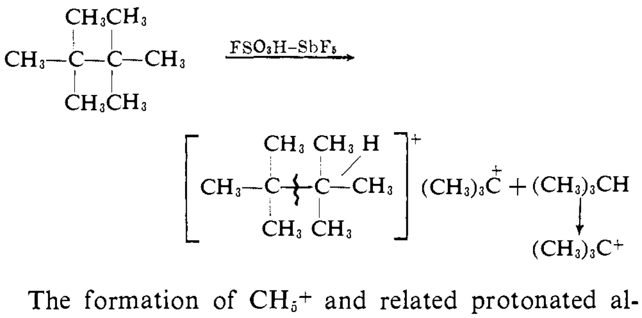
at room temperature, whereas the latter necessitates more forcing conditions. The complete exclusion of atmospheric oxygen during the experiments argues against the possibility of an oxidative process. No trace of fluorinated hydrocarbon was found, indicating the absence of radical-type fluorinating degradation.

Ethane and higher alkanes show similar reactivity in "magic acid" relating to both hydrogen exchange and "polycondensation" reactions. The intermediacy of protonated alkane-type ions is well substantiated by studies involving deuterated neopentane ($(CD_3)_4C$) and neopentane with deuterated acid (FSO_3D-SbF_5). In both cases, the methane and *t*-butyl cation formed in the reaction, as well as recovered neopentane, showed extensive hydrogen exchange. Thus neopentane is first protonated and then cleaved.



When the reaction is carried out in FSO_3H-SbF_5 diluted with SO_2ClF at lower temperatures (−30°), no protolytic cleavage reaction is observed. Instead, protonated neopentane liberates hydrogen and forms the *t*-amyl cation, obviously through fast rearrangement of the intermediate neopentyl cation. Differences in the energetics of the two cleavage reactions must be responsible for the different behavior (at different temperatures and involving different solvent systems).

The protolytic cleavage of 2,2,3,3-tetramethylbutane[2] also can be best explained by a similar mechanism.



The formation of CH_5^+ and related protonated alkanes in super acid solutions (FSO_3H-SbF_5, $HF-SbF_5$, or related acids) is remarkable. CH_5^+ is well known from mass spectroscopic studies of methane.[4] Radiation-induced polymerization of methane,[5] as well as radiolysis and photolysis of methane in the solid state,[6] was suggested to involve similar ion formation. Recently developed chemical ionization mass spectroscopy also takes advantage of the gaseous ion chemistry of methane.[7] Our observation, however, of the protonation of methane and related hydrocarbons seems to open up, for the first time, the solution chemistry of CH_5^+ and related hydrocarbon ions. The structure and chemistry of these ions, based on chemical evidence and theoretical calculations (with Professor G. Klopman), is discussed in a forthcoming full paper.

Based on the results presented in this communication and our previous work,[2] it seems appropriate to recommend that saturated hydrocarbons should be referred to only as alkanes and not as paraffins. The high chemical reactivity demonstrated by methane and other alkanes in strong acid system is no longer compatible with a name referring to "*parum affinis.*" It is, however, with some nostalgia that we make this recommendation, as "inert gases" at least maintained their "nobility" as their chemical reactivity became apparent, but referring to "noble hydrocarbons" would seem to be inappropriate.

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(4) For example, F. H. Field and M. S. B. Munson, *J. Amer. Chem. Soc.*, **87**, 3289 (1965), and references therein.

(5) D. R. Davis and W. F. Libby, *Science*, **144**, 991 (1964).

(6) P. Ansloos, R. E. Rebbart, and S. G. Lias, *J. Chem. Phys.*, **42**, 540 (1965).

(7) For a summary, see F. H. Field, *Accounts Chem. Res.*, **1**, 42 (1968).

Thermolysis and Photolysis of 3,3a,5a,6,6a,6b-Hexahydro-3,6-ethenocycloprop[*g*]indazole[1]

Sir:

Speculating on several intermediates which may be involved in valence tautomerization of $(CH)_{10}$ hydrocarbons,[2] one most often encounters the never-isolated tetracyclo[4.4.0.$0^{2,10}$.$0^{5,7}$]deca-3,8-diene (**1**).[2] In view of the recent accumulated knowledge[3] concerning the chemistry of pyrazolines, we have chosen the title compound (**2**) and its isomer (**3**) to investigate some aspects of the $(CH)_{10}$ hydrocarbon isomerization. We have synthesized **2** and wish to present a preliminary account of its chemistry.

Synthesis of 2. Bicyclo[6.1.0]nona-2,4,6-triene-*cis*-9-carboxylic acid (**4**)[4] was converted into the corresponding aldehyde which provided the tosylhydrazone **5**, mp 136–138°. The dry sodium salt of **5** underwent thermal decomposition at 90–110°, and fractional distillation of the product mixture at low temperature readily separated a pure pyrazoline (**2**) free of $C_{10}H_{10}$ hydrocarbons. Compound **2** [calculated molecular weight for $C_{10}H_{10}N_2$, 158; found (probe temperature, 75°), *m/e* 158 (intensity, *ca.* 0.5% of base peak), M − 28 (55%), M − 29 (base peak)] showed a maximum at $\lambda_{\max}^{95\%\,EtOH}$ 335 mμ (ϵ 115), $\lambda_{\max}^{CHCl_3}$ 1540 cm^{-1}. Nmr spectra of model pyrazolines and decoupling experiments permitted the following assignment of nmr signals of **2** (chemical shift in parentheses): H-6 (τ 8.05–8.35), H-5a (7.75–8.0), H-6a (7.55–7.75), H-3a (7.35–7.65), H-3 and H-6b (4.80–5.10), H-7 (located above the azo group) (4.25–4.50), H-4, H-5, and H-8 (3.85–4.25). All these spectral data including coupling constants determined are consistent with the formulation of structure **2**.[5]

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(1) We are grateful to Dr. K. L. Loening, Chemical Abstracts Service, for suggesting this nomenclature.

(2) For a list of recent publications concerning $(CH)_{10}$ hydrocarbons, see M. Jones, Jr., *J. Am. Chem. Soc.*, **89**, 4236 (1967), ref 3 and 4.

(3) R. J. Crawford and G. L. Erickson, *ibid.*, **89**, 3907 (1967), and references cited therein; W. R. Roth and M. Martin, *Tetrahedron Letters*, 4695 (1967).

(4) S. Masamune, C. G. Chin, K. Hojo, and R. T. Seidner, *J. Am. Chem. Soc.*, **89**, 4804 (1967). Dr. Loening kindly informed us that presently there are no official rules in existence to describe properly the stereochemistry of **4**. *cis* is used for simplicity. **4** was converted to cyclopropane-*cis*-1,2,3-tricarboxylic acid.

(5) All the high-field (τ 7–9) protons except *one* (H-6a) were strongly