

HIGHER COORDINATE (HYPERCARBON CONTAINING) CARBOCATIONS AND THEIR ROLE IN ELECTROPHILIC REACTIONS OF HYDROCARBONS

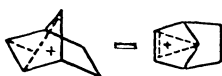
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Abstract - Experimental proof for five coordinate hypercarbon containing carbocations is reviewed and their role in hypercarbon transformations discussed. The conversion of methane and its monosubstituted derivatives into ethylene (propylene) and/or into saturated and aromatic hydrocarbons is discussed, involving both carbocationic as well as novel onium ion to ylideto olefin reactions.

The still ongoing controversy surrounding the structure of the non-classical norbornyl cation and related ions, overshadowed the significance which higher coordinate carbocations play in hydrocarbon chemistry.

First a brief summary will be presented for the extensive and compelling evidence for the existence of non-classical carbocations, i.e. five or higher coordinate carbon ("hypercarbon") containing species, the structure of which cannot be depicted by using two electron, two center (Lewis) bonding alone but also necessitates two electron, three (or multi) center bonding. Structural data presented will be mainly based on spectroscopic (NMR, ESCA) investigation of such long lived ions as



Gassman, Winstein, Olah



Winstein, Olah



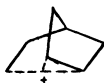
Masamune, Olah



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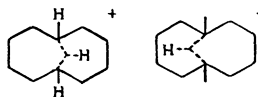
Coates



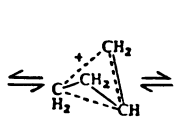
Olah



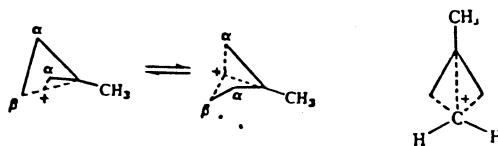
Olah, Saunders



Sorensen



Olah, Roberts



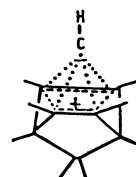
Olah, Saunders, Sorensen



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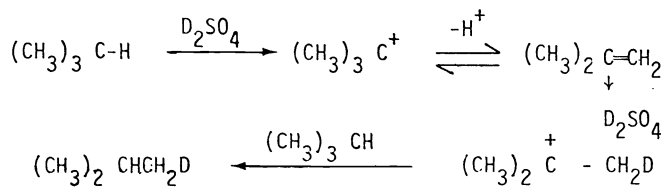
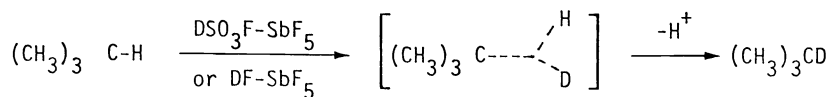


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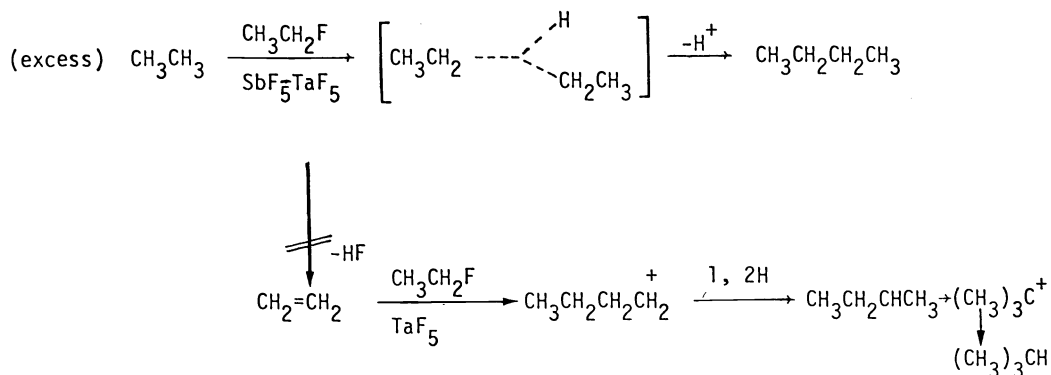
Hart

Electrophilic hydrogen-deuterium exchange of isobutane shows mainly tertiary C-H exchange at high, and primary CH_3 exchange at lower acidities. This excludes in the prior case trivalent tert-butyl cation formation, which could lead to equilibrium with isobutylene, and subsequently via reprotonation (deuteration) to CH_3 exchange:

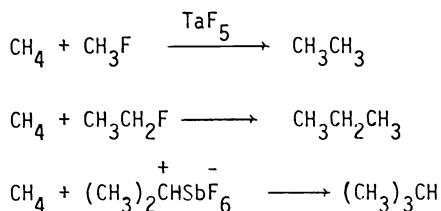


Alkylation of alkanes with alkyl cations, including the work of Siskin showing in the ethylation of ethane overwhelming formation of n-butane, exclude the possibility of intermediate ethylation of ethylene, which would lead through primary 1-butyl cation, via inevitable hydrogen and methyl shifts, to tert-butyl cation and thus isobutane.

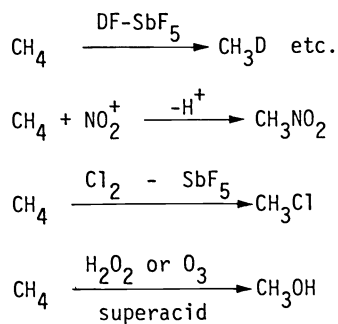
Results can be explained only with σ -alkylation of a C-H bond of ethane, leading through a five coordinate carbocation to n-butane :



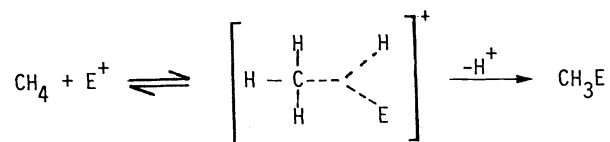
Alkylation of methane is of particular interest. $\text{CH}_3\text{F} - \text{SbF}_5$ and $\text{C}_2\text{H}_5\text{F} - \text{SbF}_5$, the corresponding TaF_5 and NbF_5 complexes, as well as alkyl cation salts readily alkylate methane. Examples to be discussed are:



Other simple electrophilic substitutions of methane, such as hydrogen-deuterium exchange, chlorination, nitration, oxygenation and the like are also carried out with ease :

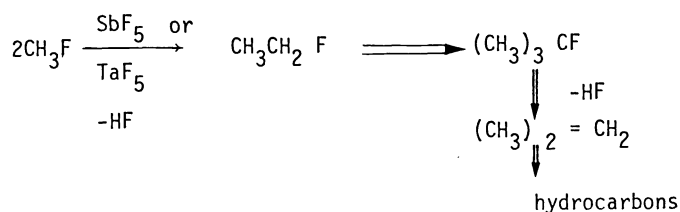


These reactions serve as prototype for electrophilic reactions of alkanes involving five-coordinate carbocations,

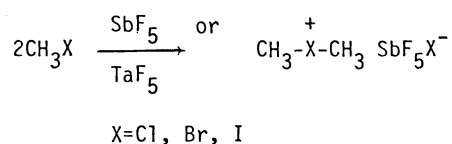


but also are of preparative significance in functionalizing methane and related higher alkanes.

In the course of our studies it was observed that methyl fluoride readily undergoes SbF_5 or TaF_5 catalyzed self condensation :

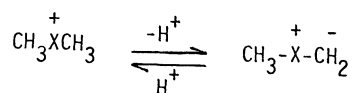


Methyl chloride, bromide and iodide undergo under similar conditions condensation to form dimethyl halonium ions,



but under more forceful conditions (150–250°C) they also undergo condensation reactions to hydrocarbons.

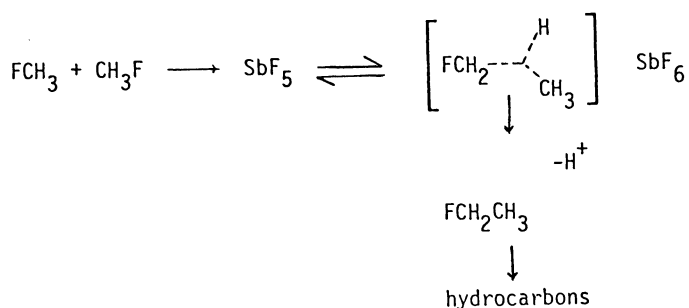
Hydrogen-deuterium exchange studies of dimethyl halonium ions indicate the formation of unstable, but reactive methylenehalonium ylides:



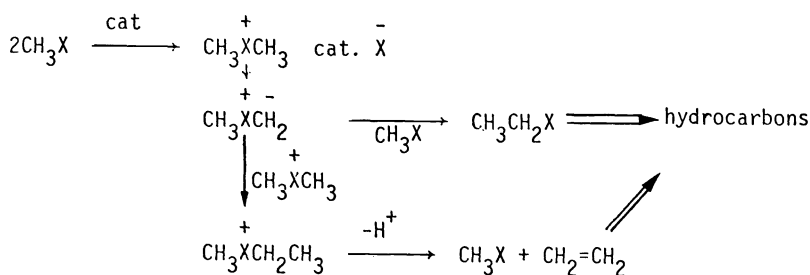
More nucleophilic gegenions facilitate deprotonation.

There are consequently two reaction paths available for the condensation reactions of methyl halides :

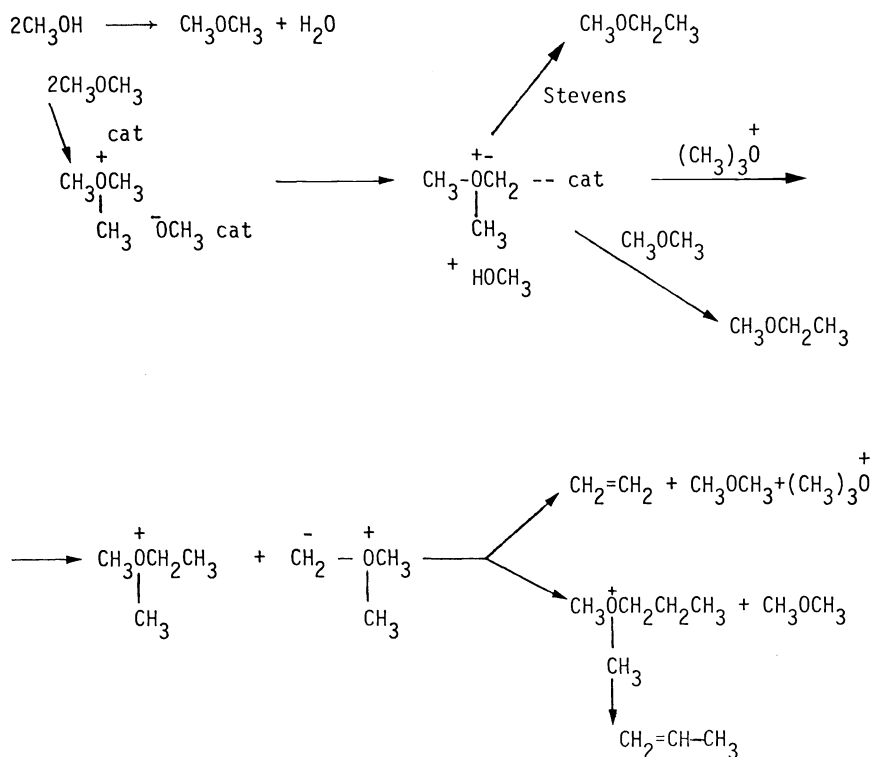
- a) σ -alkylation of a C-H bond of the methyl halide, as exemplified in the case of CH_3F where competing n-alkylation is prevented by the high electronegativity of fluorine :



- b) n-Methylation of methyl halide to initially form a dimethylhalonium ion. Proton abstraction gives a methylenehalonium ion, which then either methyleneates excess methyl halide to form ethyl halide which then readily can undergo further condensation, or is methylated to a methyl ethyl halonium ion, cleaving to ethylene:



Similar onium ion to ylide conversions, well known for ammonium and phosphonium ylides, are involved in the bifunctional acid-base catalyzed condensation reaction of methyl alcohol or dimethyl ether (or related methyl mercaptan, dimethyl sulfide, etc.) to hydrocarbons.



These reactions are catalyzed by a variety of liquid or solid acidic catalysts and are not believed to be caused by any specific shape selectivity of the catalysts, as in case of the Mobil shape selective Zeolite ZMS-5 catalyst. The acid sites promote onium ion formation, the basic sites ylide formation.

The basic reaction sequence is formation (via acid catalyzed alkylation) of onium ions, followed by base induced deprotonation to the related methylene onium ylides. These ylides being in principle solvated carbenes, can react either via alkylation on the anionic carbon or as methylenating agents. Experimental evidence is presented for both paths.

The role of five coordinate carbocations is also of substantial importance in other hydrocarbon transformations, such as isomerizations of alkanes, as well as electrophilic reactions of π -donor hydrocarbons (olefins, aromatics). Newer results and evidence to this effect will be presented, including cases of olefin additions and electrophilic aromatic substitution.

In conclusion, five and higher coordinate carbocations play an increasingly important role in preparation and transformation of hydrocarbons.

For leading references of previously published work see:

1. G.A. Olah, "Carbocations and Electrophilic Reactions", Wiley, Verlag Chemie, 1974.
2. G.A. Olah, *Chemica Scripta*, in press.