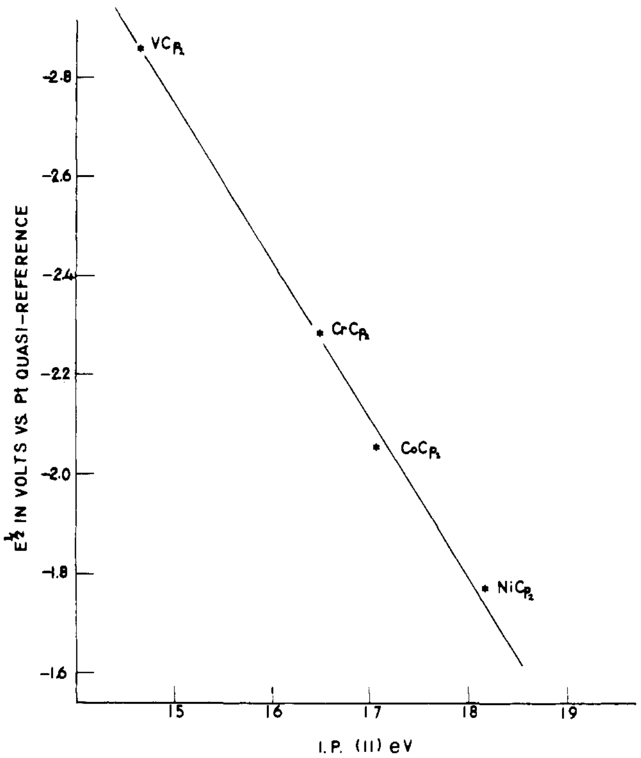

Figure 3. Plot of the polarographic half-wave potentials of the metallocene reductions as a function of second metal ionization potential.

solvent molecules would occupy the extra coordination sites in Cp_2V^{2+}. The apparently ring-parallel Cp_2V^+ is isoelectronic and isostructural with the elusive[15,16] d^2 "titanocene".

Nickelocene, which is already electron rich, can be further reduced in THF or DMF, and the anion Cp_2Ni^- can be detected by CV (Figure 2). Cp_2Ni^- has a half-life of ~1 s at room temperature. The formal Ni(I) complex, a 21-electron compound, appears to be the most electron-excessive metallocene known, since Cp_2Cu has not been reported. The anion proceeds to other electroactive products, which may include $CpNiC_5H_7$.[17]

The reduction of nickelocene ($Cp_2Ni \rightleftharpoons Cp_2Ni^-$) is abnormally slow, as shown by the large peak separations in CV measurements (Figure 2), suggesting that a structural change, possibly leading to the "slipped sandwich" structure **3**, occurs to relieve the high electron density around the metal. Such structures are well known for electron-rich metallocarboranes,[18,19] and have been predicted[20] on theoretical grounds for electron-rich metal π hydrocarbons as well.

The trend in reduction potentials of the four metallocenes known to produce simple anions (V, Cr, Co, Ni) is worth noting in that the more electron-rich metallocenes are easier to reduce. In fact a plot of $E_{1/2}$ potentials vs. the second metal ionization potential (Figure 3), is linear, as would be expected for a M(II) $\rightleftharpoons$ M(I) process. This and other points will be elaborated on in subsequent publications.

Acknowledgment. The authors are grateful to The National Science Foundation for the support of this work.

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(1) Electrochemical apparatus and procedures are similar to those reported previously (W. E. Geiger, T. E. Mines, and F. C. Senftleber, *Inorg. Chem.*, **14**, 2141 (1975)) except that the vacuum electrochemical cell has undergone a number of modifications, including one which allows loading of air-sensitive samples into the cell.

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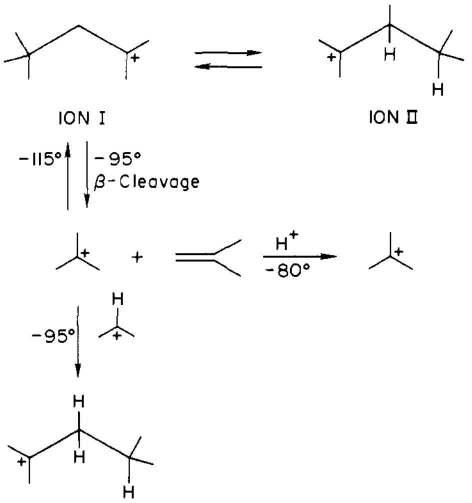
Reversible Addition of a Carbonium Ion to a Double Bond

Sir:

Addition of carbonium ions to double bonds leading to molecular adducts or ring closure is a common mechanistic step. However, detailed examination of the addition step itself has not previously been described. We report here the reaction of *tert*-butyl cation with isobutylene at −115 °C to yield dimethylneopentyl carbonium ion (I). On warming to −80 °C, **I** undergoes β-cleavage to the initial cation and olefin which may be trapped by the addition of a proton acid or isopropyl cation.



The addition of *tert*-butyl cation to isobutylene was accomplished via a modification of the molecular beam method of cation preparation.[1] The apparatus was altered so that *three* beams, one each of *tert*-butyl chloride, SbF_5, and isobutylene in a ratio of 5:10:1, impinge on the liquid nitrogen cooled surface of the evacuated apparatus. The intimate mixture formed

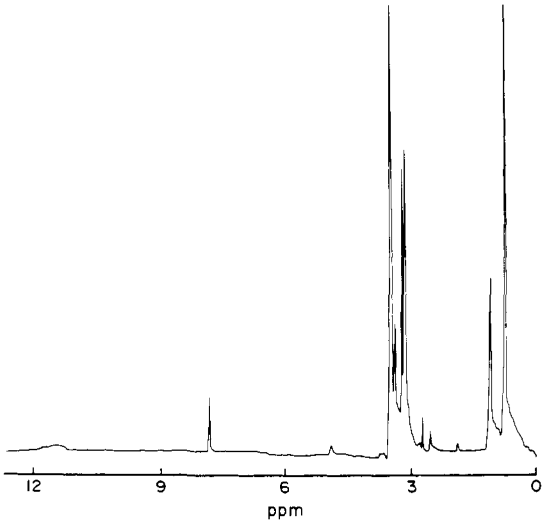


Figure 1. The 270-MHz ^{1}H spectrum of I, II, and *tert*-butyl cations in SO$_2$ClF at −110 °C.

was then dissolved in SO$_2$ClF at −125 °C. The 270-MHz proton spectrum at −103 °C demonstrated the presence of ion I and its rearrangement product ion II.[2] The resonances characteristic of ion I are 3.4 (m, 2 H), 3.1 (m, 6 H), and 1.1 ppm (s, 9 H) (external Me$_4$Si capillary).[3] Ion II had peaks at 3.2 (m, 2 H) and 1.8 ppm (m, 15). There was also a proton acid peak at 8.9 ppm. The spectrum showed no trace of further addition products of ion I with isobutylene. However, when the ratio of *tert*-butyl cation to olefin was reduced to 3:1, or when SbF$_5$ containing no proton acid was used, considerable amounts of apparent condensation products were formed.

We also prepared cation I from 2-chloro-2,4,4-trimethylpentane and excess SbF$_5$ (containing proton acid), using SO$_2$ClF as a solvent. When the sample was warmed to −80 °C it was observed that as the peaks of ion I disappeared, the acid peak also decreased at the same rate. A singlet appeared at 3.2 ppm corresponding to *tert*-butyl cation at twice the rate of decrease of ion I. These observations are explained by β-cleavage of ion I to give *tert*-butyl cation and isobutylene, which is protonated to give a second molecule of *tert*-butyl cation.

In another experiment, cation I was generated in the presence of a 5:1 excess of previously formed isopropyl cation. At −105 °C the solution (Figure 1) consists of cation I-isopropyl cation, 11.7 (heptet, 1 H) and 3.5 ppm (d, 6H), and un-ionized isopropyl chloride-SbF$_5$ charge-transfer complex 4.8 ppm[4] (heptet, 1 H) and 1.8 ppm (d, 6 H). The solution was allowed to warm in the NMR tube at −95 °C for 1 h and then returned to −105 °C (Figure 2). The spectrum shows a new resonance at 0.8 ppm. This peak corresponds to the upfield methyls of dimethylisobutyl carbonium ion. Although the other peaks of dimethylisobutyl carbonium ion occur under the doublet of the isopropyl cation and the singlet of the *tert*-butyl cation, the peak at 0.8 ppm, upon warming to −95 °C the line broadening due to the 1,3 hydride shift characteristic of this ion was observed.[5]

We feel that these observations can only be explained if isobutylene is formed as an intermediate via a β-cleavage mechanism. Oligomer or polymer is not detected since apparently the olefin is all trapped by reaction with excess isopropyl cation rather than reacting with the starting ion.

The addition of methyl fluoride-antimony pentafluoride complex[6] to isobutylene at −80 °C did not yield *tert*-amyl cation, but polymerization took place. This complex apparently does not react rapidly enough with the olefin at −80 °C to compete with reaction with the small amount of tertiary ions present.

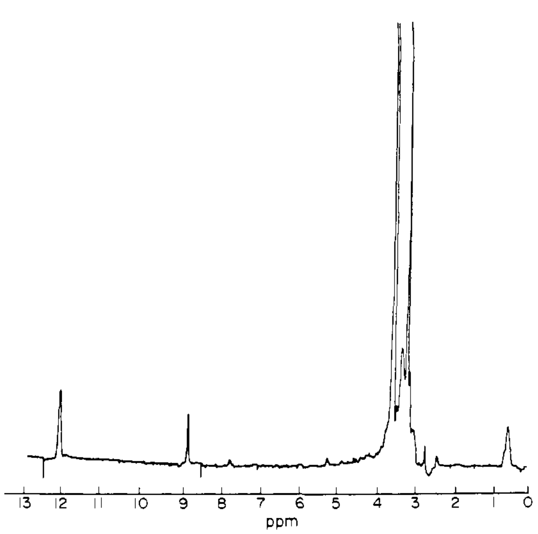


Figure 2. The 270 MHz ^{1}H spectrum of isopropyl, *tert*-butyl, and isobutyldimethyl carbonium ions at −105 °C.

A small amount of proton acid was present during the addition of isopropyl and *tert*-butyl cations to isobutylene. At −95 °C and below the cations react almost quantitatively without an observable decrease in the amount of proton acid present. The acid (presumably HF) is, therefore, less reactive than the carbonium ions in this addition reaction.

In this system, equilibrium must favor the addition step; otherwise, we would not observe it. Cleavage can be observed only because one of its products, isobutylene, is trapped.

Acknowledgment. We should like to thank the NSF for the support of this work. The NMR spectra were obtained using the Southern New England Field NMR facility sponsored by a grant from the Biotechnology Resources Program of the National Institutes of Health (RR-798).

References and Notes

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April 11, 1977

Photochemical Reaction of Alkylpentacyanocobaltates with Nitroxides. A New Biophysical Tool

Sir:

The photoinduced homolysis of the cobalt-carbon σ bond in vitamin B-12[1] and the related synthetic macrocycles[2] is well known. It was suggested by the mechanistic studies of Wood et al.[3] on vitamin B-12 that the alkyl radicals thus obtained should react readily with nitroxides and hence might provide a useful technique in spin-label studies;[4] however the restricted solubilities of these cobalt compounds ($\leq 10^{-2}$ M) limit their use in aqueous systems. We wish to report that the highly