absorption bands of the nucleic acids and polynucleotides.

We acknowledge the skillful technical assistance of M. Capecchi.[8]

(8) This work was supported by grants from the National Science Foundation and the National Cancer Institute.

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RECEIVED SEPTEMBER 19, 1960

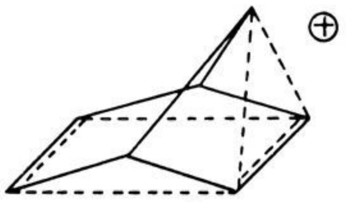
THE 7-NORBORNADIENYL CARBONIUM ION

Sir:

Recent investigations into the solvolysis of a number of norbornenyl derivatives have been characterized by the postulation of non-classical carbonium ions as intermediates. The preparation of a stable bridged carbonium ion from 7-norbornadienyl chloride has now permitted for the first time direct structural evidence to be obtained about these interesting species. Heretofore, structural evidence relating to these carbonium ion intermediates has been inferred from kinetic and product analyses. For example, the remarkable enhancement of the rate of solvolysis of *anti*-7-norbornenyl tosylate compared to the 7-norbornyl derivative has been ascribed to participation of the π electrons of the double bond to give a stabilized non-classical carbonium ion intermediate.[1] More recently, Winstein and Ordronneau[2] have reported that 7-norbornadienyl chloride solvolyzes *ca.* 10^3 faster than *anti*-7-norbornenyl chloride and suggested several possible non-classical structures for the intermediate carbonium ion. We wish to report the preparation and n.m.r. spectrum of this ion.

Treatment of 7-norbornadienol[3] with thionyl chloride in ether gave 7-norbornadienyl chloride,[2] which was dissolved in sulfur dioxide at −80° and slowly added to a similar solution of silver tetrafluoroborate.[4] The silver chloride which precipitated immediately was filtered off leaving a colorless solution. The ultraviolet spectrum at −80° showed no absorption above 330 mμ, the cut-off wave length of liquid sulfur dioxide.

The n.m.r. spectrum of this solution at −10° (Fig. 1) consists of four distinct peaks in the ratio 2:2:2:1 showing partially resolved spin-spin fine structure. We have assigned these peaks to the 7-hydrogen, the bridgehead hydrogens and two *different* pairs of olefinic hydrogens. The peak at 2.4 τ seems to consist of two overlapping triplets suggesting that the normal norbornadiene olefin triplet[5] is split by coupling with *one additional hydrogen* with coupling constant about 5 c.p.s. The above data, which definitely eliminate any symmetrical structure, are consistent with structure I, which was among those structures proposed by Winstein and Ordronneau.[2]



I

The other peaks of the spectrum can be reasonably assigned to: remaining olefin, bridgehead and bridge hydrogens, respectively. For comparison, we have determined the n.m.r. spectrum of 7-norbornadienyl chloride in sulfur dioxide. The olefinic hydrogens appear at 3.2 and 3.4 τ with the lower field peak being an incompletely resolved triplet. The bridgehead hydrogens are at 6.3 and the bridge hydrogen at 5.8.

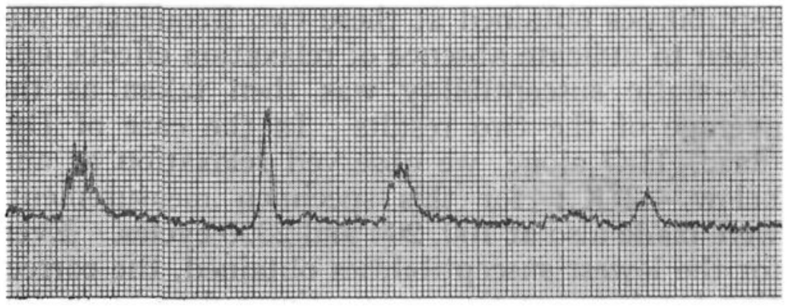


Fig. 1.—N.m.r. spectrum of 7-norbornadienyl fluoroborate in sulfur dioxide at −10°. Peak positions are given in p.p.m. relative to tetramethylsilane as 10.00.

The sulfur dioxide solution appeared to be stable at −10° but became deep brown in color on standing at room temperature for a short period. The absence of skeletal rearrangements was indicated by the exclusive conversion of the carbonium ion to the known 7-norbornadienyl acetate[3] on addition of acetic acid to the sulfur dioxide solution.

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RECEIVED OCTOBER 20, 1960

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MAGNETIC PROPERTIES OF SOME RARE EARTH CHELATES OF ETHYLENEDIAMINETETRAACETIC ACID AND ACETYLACETONE BETWEEN 1.3 AND 77.2°K.[1]

Sir:

In relation to recent studies by Grenthe and Fernelius[2] on the solution stability of a number of rare earth chelates, it was of interest to make a study of the magnetic properties of some of these compounds. The magnetic susceptibilities of the acetylacetonates of Pr, Nd, Gd, Tb, Dy, Ho, Er, Tm, and Yb, all of the same general formula $M(acac)_3 \cdot H_2O$ (prepared according to Stites, *et al.*[3]), and ethylenediaminetetraacetates of Pr, Nd and Gd of the formula $Na[M(EDTA)] \cdot 8H_2O$ (obtained from Professor T. Moeller; for preparation see

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[1] The authors wish to thank the Office of Naval Research for financial aid under Contract No. NONR 65624, and the National Science Foundation for support under Grant No. 9928.

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