that it consists of three normal methylene groups with the addition of a ring current. The experimental molar susceptibility[7] is -39.9×10^{-6}, and the methylene group susceptibility is given[8] as -11.3 to -11.9×10^{-6}, indicating an anomalous enhancement of -4 to -6×10^{-6}. The value calculated from our assumptions is -6.0×10^{-6}. Thus, the simple form of a ring-current model accounts satisfactorily for the hydrogen and carbon magnetic shieldings and the magnetic susceptibility of cyclopropane, as well as for the long-range shielding effects of three-membered rings in polycyclic compounds. There seem to be at present no empirical grounds for further refinement of the model. No quantitative theoretical justification for the assumption of a ring current has been found, nor have any other explanations for these data been proposed.

The possibility of similar effects in larger rings cannot be entirely discounted, but we have found no satisfactory way to test such a hypothesis. The differences between the carbon shieldings in cyclic hydrocarbons, including cyclopropane, and those in linear ones may be crudely fitted by a model of the form proposed for n-alkanes.[9] The effects must have a different origin, however, despite the similarity in form, because it is easy to show that reasonable bond anisotropies cannot account for the large effects found in the carbon spectra. Furthermore, the differences between the effects on carbon and hydrogen shieldings cannot be explained by an expression with the radial and angular form of that which has been proposed. Whatever the source of the effects, the existence of these differences among rings and between even large rings and straight-chain hydrocarbons demonstrates the importance of conformational factors to the shieldings.

Significant differences between the one-bond carbon–hydrogen coupling constants measured in C^{13} spectra and those measured in H^1 spectra[10] appear in Table I. A possible source of this discrepancy is the asymmetric broadening of the multiplet components in the presence of couplings among the protons. A calculation[11] was carried out on the seven-spin system $-CH_2C^{13}-H_2CH_2-$, using reasonable values for carbon–hydrogen and hydrogen–hydrogen long-range coupling constants. To simulate the subjective location of the centers of unresolved slightly asymmetric bands, the first moments of the satellite multiplets were calculated. With an assumed one-bond coupling of 124.0 c.p.s., the hydrogen spectrum gave an apparent coupling of 122.7 c.p.s. and the carbon spectrum, one of 125.7 c.p.s. The difference is in the same direction as that observed and is of about the same size.

MELLON INSTITUTE   JOHN J. BURKE
PITTSBURGH, PENNSYLVANIA

DEPARTMENT OF CHEMISTRY   PAUL C. LAUTERBUR
STATE UNIVERSITY OF NEW YORK
  AT STONY BROOK
STONY BROOK, NEW YORK

Aliphatic Dienyl Cations

Sir:

The dienylic cations I and II are stable in 96% H_2SO_4 and can be directly observed by the standard spectroscopic techniques. In contrast, cation IV has a half-life of less than 10 sec. at 25°. Addition of the dienylic alcohol III to 96% H_2SO_4 leads immediately and quantitatively to the cyclopentenyl cation V. This latter rearrangement is proving to be general and has been successful with homologs of III in which ethyl and isobutyl replaced the methyl at C-1. The cation V was identified by its characteristic n.m.r. spectrum.[1]
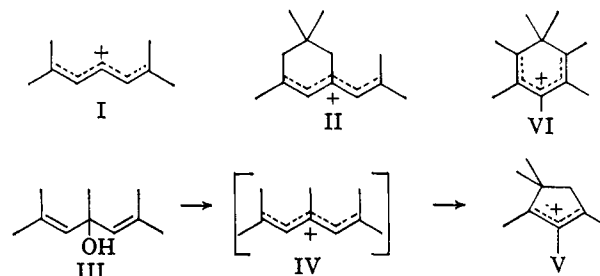
Previously there has been one isolated example of the direct observation of a dienylic cation of the type which is in equilibrium with an aliphatic triene. Doering, Saunders, and the group at Humble Oil Company discovered the heptamethylcyclohexadienyl cation (VI) as a product of exhaustive methylation of benzene.[2] Cation VI is half-formed at approximately a pH of zero. Cations I and II are probably of similar stability although chemical instability in the more dilute acids prevented accurate evaluation. It is certain that the half-formation point is below 50% H_2SO_4.

A number of cyclohexadienyl cations which were formed by protonation of benzene derivatives have been directly observed. The classic paper of MacLean and Mackor[3] reports the n.m.r. spectra of a number of such ions, including those formed by protonation of toluene, mesitylene, and hexamethylbenzene. The stability of the benzene ring necessitates high levels of acidity in order to produce these cations. MacLean and Mackor used HF–BF$_3$, and Olah and co-workers[4] have observed similar spectra in HF–SbF$_5$. The most basic of these alkyl benzenes is hexamethylbenzene and this is half-protonated in 92% H_2SO_4.[5]

(7) J. R. Lacher, J. W. Pollock, and J. D. Park, *J. Chem. Phys.*, **20**, 1047 (1952).

(8) P. W. Selwood, "Magnetochemistry," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1956, p. 94.

(9) E. G. Paul and D. M. Grant, *J. Am. Chem. Soc.*, **85**, 1701 (1963).

(10) C. S. Foote, *Tetrahedron Letters*, **9**, 579 (1963).

(11) The Frequint IV program, written by Dr. A. A. Bothner-By of Mellon Institute, was employed.

(1) N. Deno, H. G. Richey, Jr., N. Friedman, J. D. Hodge, J. J. Houser, and C. U. Pittman, Jr., *J. Am. Chem. Soc.*, **85**, 2991 (1963).

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(3) C. MacLean and E. L. Mackor, *Mol. Phys.*, **4**, 241 (1961).

(4) G. Olah and co-workers, unpublished results of the Dow Chemical Company.

(5) N. Deno, P. T. Groves, and G. Saines, *J. Am. Chem. Soc.*, **81**, 5790 (1959).
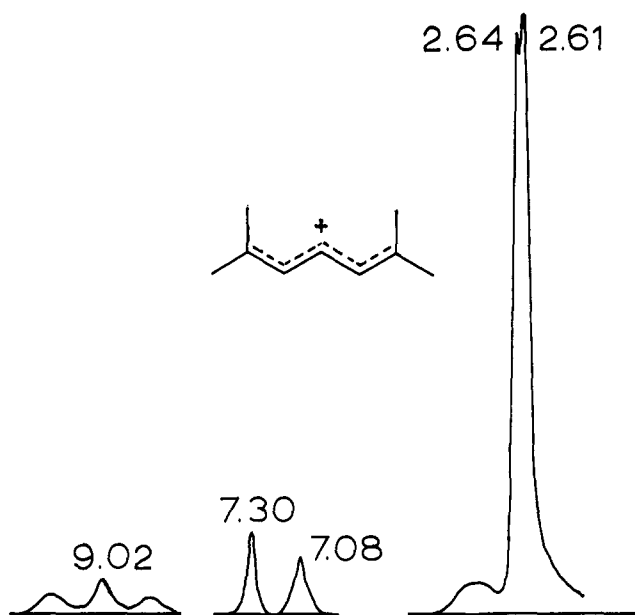
The n.m.r. spectrum of I (Fig. 1) is particularly satisfying. The H at C-4 is at 9.02 p.p.m. [downfield from $(CH_3)_4Si$]. This is farther downfield than the two hydrogens at C-3 and C-5 (7.19 p.p.m.), in accord with the MO estimate that a +0.33 charge resides on C-4 but zero charge on C-3 and C-5. The separate bands for the two pairs of methyl groups indicates that the methyl groups do not equilibrate by rapid rotation about the C=C bond and that cis–trans isomerism is possible in the dienyl cations as had been found in the alkenyl cations.[1] The position of the methyl bands at 2.61 and 2.64 p.p.m. is at slightly higher fields than the 2.95 and 2.97 p.p.m. found for the methyl groups in the 2,4-dimethylpentenyl cation, in accord with the expectation that the positive charge is more diffuse in the dienyl cations.

The n.m.r. spectra of I and II (Fig. 2) are similar in band positions to the spectrum of VI, and to the spectra of the protonated benzene derivatives, confirming that the protonated aromatics are simple aliphatic dienyl cations. Such a view is further supported by the ultraviolet spectrum of I [λ_{max} 397 mμ (ϵ 9900)] and II [λ_{max} 395 mμ (ϵ 47,000)] which are similar to the spectra of the protonated benzenes[6,7] and in agreement with the $\sim$400 mμ λ_{max} predicted by simple MO theory.

The solution of I in H_2SO_4 was produced by H_2SO_4 extraction of 2,6-dimethyl-1,3,5-heptatriene from solution in CCl_4. The triene was produced in 72% yield by reduction of phorone with $LiAlH_4$.[8] The solution of II was similarly produced from the triene (or mixture of trienes) obtained by addition of $CH_2=C(CH_3)-CH_2MgBr$ to isophorone. The Grignard reagent, though of the allylic type, was formed by the standard procedure, and the yield of triene was perhaps 40%, although contamination by dienylic alcohol and iso-
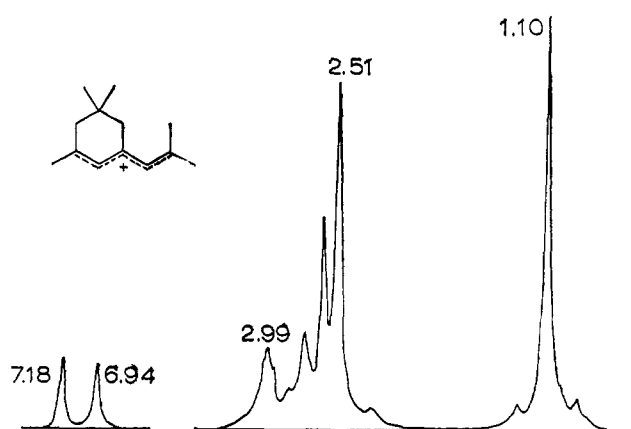
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Fig. 2.—N.m.r. spectrum of II in 96% H_2SO_4.

phorone (removed by treatment with hydroxylamine) prevented accurate estimate of the yield. The solution of V was produced by addition of III to H_2SO_4; and III was prepared by addition of CH_3MgBr to phorone.[5] The addition is entirely 1,2 whereas C_2H_5MgBr adds partially 1,4. Fortunately, C_2H_5Li gave 1,2-addition.

The triene derived from I can be quantitatively regenerated from I by rapid dispersal[1] of the H_2SO_4 solution into 10% aqueous NaOH. The n.m.r. spectrum of the triene, initial and recovered, agrees with that expected for 2,6-dimethyl-1,3,5-heptatriene.

There appears to be only one valid report of direct observation of a polyenylic cation (in equilibrium with an aliphatic polyene) higher than dienylic, and this was the complex C-22 tetraenylic cation elucidated by de Vries.[9] The work reported herein suggests that a wide variety will soon be observed.

(9) L. de Vries, J. Am. Chem. Soc., 83, 2392 (1961).

DEPARTMENT OF CHEMISTRY   N. C. DENO
THE PENNSYLVANIA STATE UNIVERSITY
UNIVERSITY PARK, PENNSYLVANIA   CHARLES U. PITTMAN, JR.
            RECEIVED DECEMBER 6, 1963

The Crystal and Molecular Structure of β-Adenosine-2'-β-uridine-5'-phosphoric Acid[1]

Sir:

Although the crystal structures of a number of nucleosides and mononucleotides have been determined, no precise single-crystal analyses of the detailed molecular geometry of any dinucleotides or other polynucleotides have been reported. The conformation and packing of such molecules is of significance in connection with hypotheses about the molecular geometry and conformations important in the mechanisms of reactions involving nucleic acids and related species. We were fortunate in obtaining good single crystals of a dinucleoside phosphate, β-adenosine-2'-β-uridine-5'-phosphoric acid (I), from Dr. A. M. Michelson, and have determined its detailed structure by X-ray methods. Although this is not a naturally occurring