field opposes the applied magnetic field directly above and below the aromatic ring and thus produces the observed strong shielding effect on the protons of the base and the lithium cation.

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Alkynyl Cations

Sir:

This communication reports the first direct observations of alkynyl cations (**1**). A particularly interesting aspect of these cations is that they can also be regarded as vinyl cations if resonance structure **1b** is important.
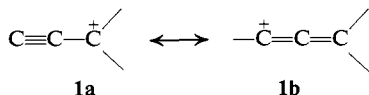
Solutions of propynyl-di-*p*-methoxyphenylcarbinol[1,2] (**2**) in concentrated sulfuric acid exhibited λ_{max} 518 mμ (ϵ 43,000), indicating that a new absorbing species
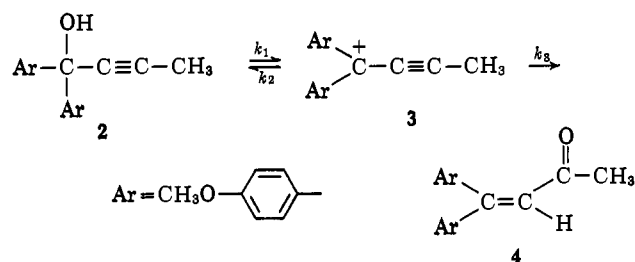
had formed. Careful introduction of **2** into concentrated sulfuric acid by extraction from carbon tetrachloride gave solutions that exhibited the simple n.m.r. spectrum[3] shown in Figure 1. This spectrum is assumed to be due to carbonium ion **3**; the assignment for each band is indicated in the figure. Structure **3** for the new species in the solutions seems reasonable because of the close correspondence of the positions of the bands due to the *p*-methoxyphenyl group with those of other *p*-methoxyphenyl-substituted carbonium ions.[5] Strong confirmation of structure **3** was obtained by recovery of the starting alcohol (**2**) on neutrali-

(1) This alcohol was prepared by addition of propynyllithium to di-*p*-methoxyphenyl ketone.

(2) A satisfactory analysis was obtained for this new compound.

(3) Chemical shifts are expressed in p.p.m. relative to tetramethylsilane as 10.00. Tetramethylammonium chloride, used as an internal reference in the sulfuric acid solutions, was assumed to absorb at 6.90 p.p.m.[4]

(4) N. C. 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).

(5) R. B. Moodie, T. M. Connor, and R. Stewart, *Can. J. Chem.*, **37**, 1402 (1959); P. von R. Schleyer, D. C. Kleinfelter, and H. G. Richey, Jr., *J. Am. Chem. Soc.*, **85**, 479 (1963); H. G. Richey, Jr., unpublished observations.
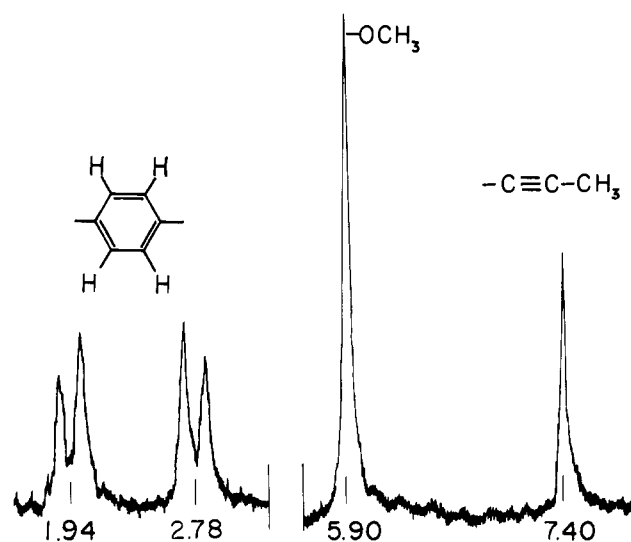
Figure 1. N.m.r. spectrum of a sulfuric acid solution of cation 3.

zation of the sulfuric acid solutions by their careful addition to aqueous sodium hydroxide using a rapid dispersal technique. The recovered products, obtained in yields of about 90%, consisted principally of alcohol **2**, though an isomer, ketone **4**,[2,6] always constituted at least 10% of the product. This ketone formed almost quantitatively when dilute perchloric acid was added to an acetone solution of **2**. Under conditions that allow equilibrium to be reached, **4** is the product formed from reaction of water with solutions of the ion; however, irreversible reaction of the ion with water leads principally to **2**, so k_2 must be larger than k_3.

The n m.r. absorption of the propynyl methyl group of ion **3** is considerably downfield from the absorption at 8.13 p.p.m. exhibited by this group in a carbon tetrachloride solution of **2**. This is probably a result of significant delocalization of charge into the propynyl group as suggested by resonance structure **1b**. The basicity of **2**, which would indicate the effect of delocalization into the propynyl group on stabilization of cation **3**, could not be measured directly because of the rapid disappearance of the ion in more dilute solutions of sulfuric acid, presumably due to attack by water leading to **4**. In 77% sulfuric acid, the half-time for the disappearance of the 518 mμ absorption of **3** was 45 min. at ~25°. The disappearance became very much more rapid as the acidity was lowered; in 20–50% sulfuric acid, the concentration range in which the concentrations of **2** and **3** might be expected to become comparable, the color of the ion could be seen but faded within seconds.

Addition either of **5**[7] or a mixture[8] of **7** and **8** to concentrated sulfuric acid led to solutions which exhibited the n.m.r. spectrum shown in Figure 2. This

(6) Ketone **4**, b.p. 180–185° (0.12 mm.), formed a 2,4-dinitrophenylhydrazone derivative,[2] m.p. 181–182°. The n.m.r. spectrum of a carbon tetrachloride solution of **4** exhibited absorptions at 8.27 (singlet, 3 H) for the C-methyl hydrogens, 6.27 (singlet, 3 H) and 6.23 (singlet, 3 H) for the O-methyl hydrogens, 3.68 (singlet, 1 H) for the vinyl hydrogen, and 2.78–3.36 p.p.m. (2 overlapping quartets, 8 H) for the aryl hydrogens.

(7) Alcohol **5**, b.p. 80–85° (2.2 mm.), was obtained by addition of a propynyl Grignard reagent to isophorone.

(8) A mixture of hydrocarbons, b.p. 55–65° (1.7 mm.), of which 7 and 8 are probably the major components, was also obtained by addition of a propynyl Grignard reagent to isophorone.
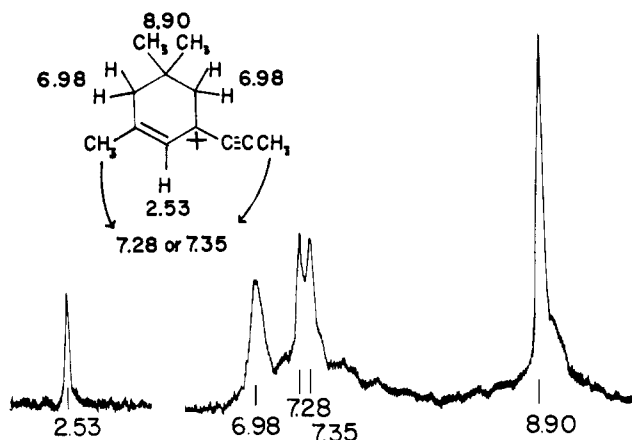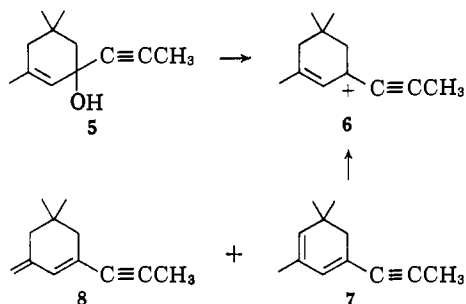
Figure 2. N.m.r. spectrum of a sulfuric acid solution of cation 6.

spectrum is assumed to be due to cation **6**; the peak assignments agree closely with those reported[4] for other carbonium ions containing a cyclohexenyl system. The absorption of the hydrogens of the propynyl methyl group (which must be either at 7.28 or

7.35 p.p.m.) is considerably downfield from the absorption of the same group at 8.22 in **5** and at 8.07 p.p.m. in the mixture of **7** and **8**. In fact, the magnitude of the downfield shift of the absorption due to this group is about the same in the formation of **3** and of **6**.

Acknowledgment. We are grateful to the National Science Foundation for a grant in support of this work and also for providing funds to aid in the purchase of the Varian A-60 n.m.r. spectrometer used in this research.

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Hydrogen Participation in cis-4-t-Butylcyclohexyl Brosylate Solvolysis

Sir:

In a previous communication we reported a strong conformational dependence of cis-4-t-butylcyclohexyl p-bromobenzenesulfonate (brosylate), I.[1] It was then suggested that the large *axial* β-effect, though in accord with the hyperconjugation postulate,[2] might be due to

(1) V. J. Shiner, Jr., and J. G. Jewett, *J. Am. Chem. Soc.,* **86,** 945 (1964).
(2) V. J. Shiner, Jr., and J. S. Humphrey, Jr., *ibid.,* **85,** 2416 (1963).

neighboring hydrogen participation which we, and others,[3] view as an extreme manifestation of a type'of electronic interaction also associated with hyperconjugation. In order to resolve this question, we have determined the effect of substitution of deuterium for *each* of the four β-hydrogen atoms on the rate of solvolysis of I.

cis-4-t-Butylcyclohexanol-1-*d* and cis-4-t-butylcyclohexanol-cis-2-*d* (equatorial β-deuterium) were prepared as previously described.[1] cis-4-t-Butylcyclohexanol-2,2,6,6-d_4 was prepared by base-catalyzed exchange of 4-t-butylcyclohexanone with deuterium oxide followed by reduction with lithium aluminum hydride and separation of the axial and equatorial alcohols by elution chromatography and preparative v.p.c. Pyrolysis of a mixture of cis- and trans-4-t-butylcyclohexyl-2,2,6,6-d_4 acetate afforded 4-t-butylcyclohexene-2,6,6-d_3. Hydroboration of this olefin followed by hydrogen peroxide oxidation and the previously described[1] separation procedure afforded cis-4-t-butylcyclohexanol-trans-2,6,6-d_3 (axial,axial,equatorial β-deuterium). cis-4-t-Butylcyclohexanol-cis-2,6,6-d_3 (axial,equatorial,equatorial β-deuterium) was obtained by epoxidation of this olefin followed by lithium aluminum hydride reduction and the previously described[1] separation procedure. Combustion and n.m.r. analysis indicated that the alcohols were about 98% isotopically pure. The brosylates of the various alcohols were prepared by the usual Tipson procedure.[4]

The products of aqueous ethanolysis of ester I consisted of 86% t-butylcyclohexene, 3% ethers, 9% trans-4-t-butylcyclohexanol, and 2% (axial) t-butylcyclohexanol (probably a mixture of 3 and 4 alcohols).[1] Complete deuteration of the β-positions did not substantially lower the olefin fraction of the product. Infrared analysis of the olefin fraction from the solvolysis of cis-4-t-butylcyclohexyl-trans-2-*d* brosylate indicated that the olefin-forming step of the reaction involves the loss of an axial (*trans*) β-hydrogen atom.

The rate data, collected in Table I, were obtained as previously described.[1] The precision of the conductometric method is ±0.1%.

Table I. Solvolysis Rates of Deuterated
cis-4-t-Butylcyclohexyl Brosylates[a]

Deuteration[b]	$k_1 \times 10^4$, sec.$^{-1}$	k_H/k_D
None	3.938	
α-Deuterium, e	3.275	1.202
β-Deuterium, a	2.743	1.436
β-Deuterium, e	3.593	1.096
β-Deuterium (3), a, a, e	1.535	2.565
β-Deuterium (3), a, e, e	2.207	1.784
β-Deuterium (4), a, a, e, e	1.376	2.862

[a] Aqueous ethanol (50 vol. %) at 35°. [b] a = axial, e = equatorial.

(3) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *ibid.,* **74,** 1113 (1952).
(4) R. S. Tipson, *J. Org. Chem.,* **9,** 235 (1944).

It is clear from these data that successive β-deuterium substitution at conformationally equivalent sites does not lead to cumulative isotope effects, *i.e., the solvolytic rate retardation caused by 2,6-diaxial deuteration exceeds the square of that caused by monoaxial deuteration* ($2.565/1.096 = 2.339 > 2.062 = 1.436^2$). It should be