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SYNTHESIS AND PROTON MAGNETIC RESONANCE SPECTRA OF SOME BENZTRICYCLO [3.2.1.$0^{2,4}$] OCTENES. AN UNUSUALLY LARGE STERIC DESHIELDING EFFECT[1]

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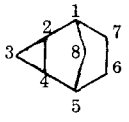
The molecular geometries of the bridged tricyclic systems I, II and III are uniquely suited for investigation of homoconjugative effects of a fused cyclopropane ring relative to a double bond or benzene ring in carbonium ion or radical processes at the bridge (C-8) position[2]. Since the stereoelectronic requirements of the cyclopropane ring should be of consequence for effective participa-



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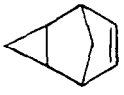

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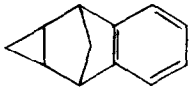
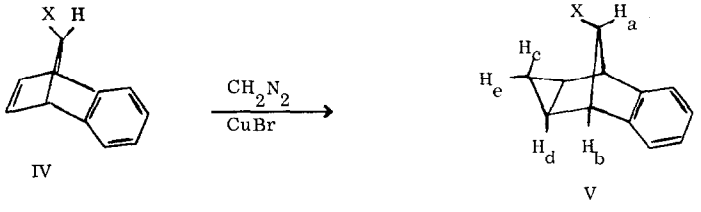


III

tion[3], a study of relative reactivities of bridge substituted exo and endo derivatives of these tricyclic systems is of considerable interest. In the course of such a study, we have prepared a series of exo-anti-8-substituted derivatives of benztricyclo [3.2.1.$0^{2,4}$] octene (III) and have examined their proton magnetic

resonance spectra in some detail. We now wish to report our synthetic and spectral results together with a description of some unusually large (1-2 p.p.m.) steric deshieldings of a cyclopropyl proton by oxygen functions. This deshielding effect should be of general use in the assignment of configuration in 8-substituted tricyclo [3.2.1.$0^{2,4}$] octane derivatives.

Treatment of anti-7-benznorbornadienol (IV-OH)[4] with excess diazomethane in the presence of cuprous bromide[5] afforded exo-anti-8-benztricyclo [3.2.1.$0^{2,4}$] octenol (V-OH)[6], m.p. 147-148°, in almost quantitative yield.* The infrared spectrum was consistent with the proposed structure showing O-H stretch at 2.72 μ and a weak cyclopropyl absorption at 9.52 μ in addition to bands characteristic of the benznorbornene system. More convincingly, the n.m.r. spectrum (Table I) showed a 4 proton A_2B_2 multiplet at τ2.89, a broad one proton multiplet at 6.51 for the bridge hydrogen (H_a), an incompletely resolved 2 proton doublet at 6.63 for the bridgehead protons (H_b), a complex one proton multiplet (sextuplet) at 7.37 assigned to H_c, a one proton singlet at 7.94 for the hydroxyl proton, and a complex 3 proton multiplet centered at 8.99 which was assigned to the remaining

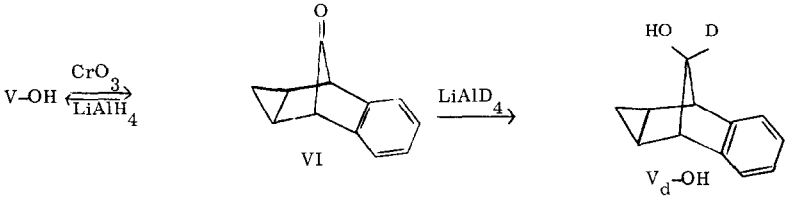


IV V

cyclopropyl protons H_d, H_e. The striking feature of this spectrum is the selective deshielding of one of the cyclopropyl protons. Assuming an exo configuration, which was established as shown below, the only reasonable assignment for

*All attempts at cyclopropanation of either IV-OH or 7-norbornadienol by the Simmons-Smith procedure were unsuccessful. This result is somewhat surprising considering the well-known activating influence of a neighboring cis (syn) hydroxyl function in this reaction [7].

the deshielded proton is H_c. Decoupling experiments, although only partially successful, supported the assignments [8].

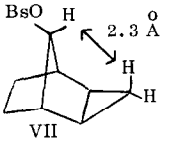


Oxidation of V-OH with CrO_3-sulfuric acid in acetone solution gave the corresponding ketone VI[6], m.p. 77-78°, carbonyl stretch at 5.65 μ. In contrast to the alcohol V-OH the chemical shifts of four cyclopropyl protons of VI appeared quite normal (Table I). This ketone was quantitatively converted back to V-OH by any of several reducing agents including sodium borohydride, lithium aluminum hydride, and lithium in liquid ammonia-ethanol solution. Reduction of VI with lithium aluminum deuteride led to the deuterated alcohol V_d-OH(H_a=D). The n.m.r. spectrum of the latter material was virtually identical to that of the undeuterated alcohol with the exception that the τ6.51 multiplet was absent and the bridgehead protons H_b now appeared as a sharp singlet ($\omega_{1/2}h$=1.75-1.80 c.p.s.). The observed lack of coupling between bridgehead protons H_b and H_d clearly establishes the exo configuration for the cyclopropane ring[9].

The configurations of the benzoate V-OBz[6], m.p. 96-97°, and the t-butyl ether V-OtBu[6], m.p. 77-78°, prepared by cuprous bromide-diazomethane cyclopropanation of the corresponding benznorbornadienes, were conveniently established as exo-anti by their n.m.r. spectra, each showing a well-deshielded cyclopropyl proton resonance at τ7.5 ± 0.2. A similarly shifted low field signal was observed in the spectra of the methyl ether and brosylate derivatives V-OMe[6], m.p. 56-58°,

and V-OBs[6], m.p. 129-130°, prepared from V-OH by standard procedures. In contrast no unusual chemical shifts were noted for the cyclopropane hydrogens of the parent hydrocarbon V-H[6], m.p. 35-37°.

The large deshielding effects observed in these tricyclic systems apparently arise largely from severe van der Waals interactions between proton H_c and the oxygen substituents at C-8[10,11], although other factors associated with the polarity and anisotropy of the substituent groups may contribute. From an X-ray crystallographic analysis of the tricyclooctane derivative VII[12] Pincock[13] has estimated the hydrogens at carbon atoms C-3 and C-8 to be about 2.3Å apart. Assuming a similar geometry for V-H this leads to a van der Waals compression factor of $\underline{c}$=0.1[14] which suggests some deshielding of H_c even in the hydrocarbon.* Introduction of a bulkier substituent than hydrogen at C-8 (or C-3) should increase the steric compression and resultant deshielding effect on the remaining proton H_c.



VII

As seen from Table I the magnitude of the deshielding effect on H_c, $\Delta\delta$, varies with the nature of the oxygen function in the order $\underline{Ot}$Bu > OH~OMe > OBz > OBs, which is essentially the order of decreasing electron density at the oxygen atom. This result is in accord with the suggested deshielding mechanism since van der Waals repulsion between the oxygen and C-H_c charge clouds should distort the electronic environment of H_c and lead to a low-field shift for this proton[15]. In line with this, calculations have shown[16] that the paramagnetic shifts produced by the electric field of neighboring non-bonded polar groups are proportional to the

*A detailed analysis of the rather complex spectrum of hydrocarbon V-H would be required in order to uncover this apparently small effect.

TABLE I

Proton Chemical Shifts of exo-Benztricyclo [3.2.1.$0^{2,4}$] Octene Derivatives[a]

Compound	Chemical Shift (τ)						
	Aromatic[b]	H_b	H_a	H_c	H_d, H_e[c]	Other	$\Delta\delta$[d] (p.p.m.)
V-H	2.94	6.83(b)	———	8.67(m)[e] 9.13(m)	———	-	-
V-OH	2.89	6.63(d)	6.51(m)	7.37(sx)	8.99	7.94(s)	1.62
V-OBz	2.01[f] 2.71	6.40(d)	5.54(m)	7.66(sx)	8.91	-	1.25
V-OtBu[g]	2.84	6.72(b)	6.80(b)	7.26(sx)	9.05	8.84(s)	1.79
V-OMe[g]	2.87	6.52(d)	6.96(m)	7.47(sx)	9.03	6.74(s)	1.56
VI	2.69	6.54(s)	- ———	8.57(m)[e] 8.85(m)	———	-	-
V-OBs	2.30[h] 2.86	6.49(d)	6.04(b)	7.72(m)	8.88(m)	-	1.16

a. Recorded in deuterochloroform on a Varian A-60A or DP-60 instrument with tetramethylsilane as internal reference; multiplicities represented by s(singlet), d(doublet), sx(sextuplet), m(multiplet), b(broad singlet); relative peak areas were in accord with assigned structures.

b. An A_2B_2 pattern observed unless otherwise noted.

c. Measured as the center of the A_2B-part of an A_2BX multiplet.

d. Difference in chemical shift between H_c and the center of the H_d, H_e multiplet.

e. Estimated centers of complex overlapping multiplets.

f. Ester phenyl ortho protons.

g. The spectrum in carbon tetrachloride is virtually identical to that reported here suggesting that there is no significant solvent shift for these compounds in deuterochloroform.

h. Four protons of the ester phenyl.

field strength. The larger shift observed for V-OtBu, as compared to V-OMe, can be explained not only by the enhanced inductive effect of the t-butyl group, but also by a conformational effect that, on the average, places the oxygen atom of V-OtBu closer to the plane of the cyclopropane ring.

Subsequent reports will detail the chemistry of these and related tricyclo [3.2.1.$0^{2,4}$] octane derivatives, including the results of a solvolytic study of V-OBs.

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