The Stereochemistry of the Bicyclo[3.2.1]octane System. IV.[1,2] Some Long-Range Couplings of Vinyl and Allylic Protons
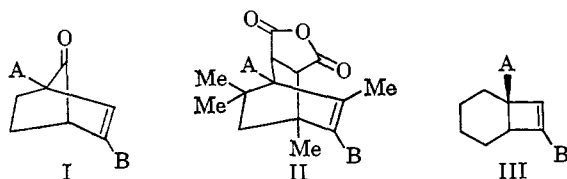
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The nuclear magnetic resonance spectra of exo-1-methyl-3,4-dibromobicyclo[3.2.1]octene-2 (IV), exo-3,4-dibromobicyclo[3.2.1]octene-2 (V), exo-3-bromo-4-hydroxybicyclo[3.2.1]octene-2 (VI), and 3-bromobicyclo-[3.2.1]oct-2-en-4-one (VII) were studied by the double resonance method. It was shown that although the bicyclo[3.2.1]octene-2 skeleton permits the operation of three kinds of long-range coupling (W-plan, homoallylic and allylic), only the first two types were actually observed. The reasons for this behavior are discussed.

Introduction

Recently, the taxonomy of long-range coupling of vinyl and allylic protons has received attention.[5,6] There appear to be two classes of long-range coupling involving vinyl protons which may be regarded as anomalous. The first class comprises those cases where coupling is observed between vinyl and allylic bridgehead protons in bicyclic olefins (*e.g.*, J_{AB} = 2.4 in I and 1.4 c.p.s. in II), but nevertheless difficult to picture in terms of an interaction mechanism. The second class consists of those compounds where coupling between vinyl and allylic protons is unobserved, but expected on the grounds of a suitable geometry for their interaction. An example of this is found in III.[7] In III, proton A projects axially to the plane of the double bond and the vinyl proton B thereby forming a spatial relationship which has appeared to be necessary in many cases for observable vinyl–allylic proton coupling.

We now wish to report a new category of long-range coupling by vinyl and allylic protons, where at first sight the geometry appears to be suitable on a σ–π interaction basis,[8] but in fact the protons in question do *not* couple with each other (or only negligibly so), but couple with a remote proton elsewhere in the molecule. This new category is exemplified by the behavior of the bicyclo[3.2.1]octene-2 structures IV–VII.[1]

Results and Interpretation

The vinyl protons B in all four molecules (IV–VII) show additional fine structure, which is due to interaction with a remote proton; the values of this additional coupling are 1.4, 1.0, 0.9, and 1.4 c.p.s., respectively. Moreover, the corresponding allylic protons A exhibit fine splittings of 0.4, 0.6, and 0.6 c.p.s.; but quite obviously, not of the same magnitudes as those of the vinyl protons. Therefore, there is no observable *mutual* vinyl–allylic coupling. This fact is emphasized by the doubled doublet of the vinyl signal of VII which has no allylic proton.
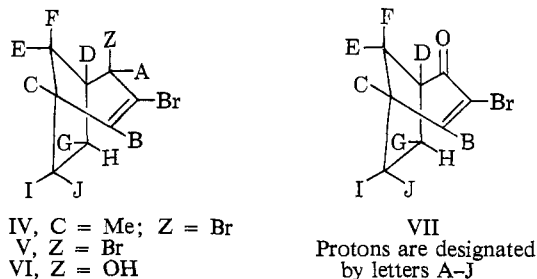
IV, C = Me; Z = Br
V, Z = Br
VI, Z = OH

VII
Protons are designated by letters A–J

The proton responsible for the additional multiplicity of the vinyl and allylic resonances (designated X), was elucidated by application of the double resonance method.[9]

For the first and clearest illustration, the results obtained with *exo*-1-methyl-3,4-dibromobicyclo[3.2.1]-octene-2 (IV) are discussed. The 60-Mc. n.m.r. spectrum of IV together with the first-order analysis of the vinyl, allylic, and bridgehead protons is depicted in Figure 1.

The analysis of the vinyl and allylic protons is simple. The septulet exhibited by the sole bridgehead proton D is due to the coupling of D with E, G, and A. The contribution from protons F and H may be regarded as negligible since a Dreiding model[10] of IV indicates that the dihedral angles between D and F and D and H are very nearly 90°. Clearly, the coupling constant of 2.8 c.p.s. is ascribable to J_{DA} and on the basis of the dihedral angles for protons D and E (40°) and D and G (27°), the values of 5.0 and 7.0 c.p.s. may be attributed to J_{DE} and J_{DG}, respectively.[11] From the total set of 12 protons, the vinyl and allylic protons B and A

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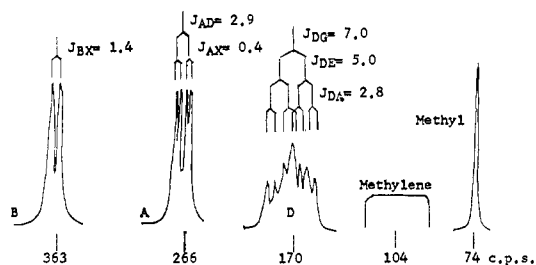(11) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

Figure 1. The 60-Mc. spectrum of IV in CCl₄ solution.

Figure 2. Signal simplification of IV during irradiation.

can be rejected and also the protons of the methyl group as it appears as a sharp singlet. Thus one (or possibly two) of the remaining seven protons D, E, F, G, H, I, or J has to be proton X. Figure 2 shows what happens to the signals of B, A, and D in different double resonance experiments.[12]

Irradiation of the bridgehead proton D leaves the vinyl resonance unchanged and causes the allylic signal to collapse to a closely spaced doublet ($J = 0.4$ c.p.s.) which shows that D cannot be X (Figure 2a).

Irradiation of the allylic proton A leaves the vinyl signal unaltered (and confirms that A or B cannot be X), but simplifies the bridgehead septulet to a quartet of spacings of 5.0 and 7.0 c.p.s., where D is now only coupled to E and G (Figure 2b).

Irradiation in the upfield portion of the methylene massif at 85 c.p.s. (from TMS) brings about informative changes. The bridgehead resonance D has become a quartet of spacings of 7.0 and 2.8 c.p.s., on account of the decoupling of E. Moreover, this decoupling of E has divested the vinyl and allylic signals of their fine structure so that a singlet and a widely spaced doublet (2.8 c.p.s.) result, respectively (Figure 2c). Consequently, the coincidence of these two changes provides strong evidence that proton E is indeed X.

Nevertheless, there is the possibility that during the decoupling of E, another proton, say X, is decoupled simultaneously. Since the range of irradiating frequency needed and used to collapse a specific signal is quite narrow (± 3.0 c.p.s.) the aforementioned possibility is correspondingly small. So if a proton, other than E, should be responsible for the long-range effect, then it will be one which has a closely similar chemical shift to that of E.

Double resonance experiments were also carried out on exo-3,4-dibromobicyclo[3.2.1]octene-2 (V), its exo-4-hydroxy analog (VI) and 3-bromobicyclo[3.2.1]oct-2-en-4-one (VII) with similar results as were obtained with IV. However, the presence of an extra, different bridgehead proton C in structures V, VI, and VII constitutes a feature which enabled the identity of proton E with X to be established unequivocally. The argument based on the n.m.r. spectrum of VII will be used.

The 60-Mc. spectrum of VII (Figure 3) shows the vinyl proton B as a doubled doublet due to its coupling with the bridgehead proton C and with another proton X ($J_{BC} = 7.0$ and $J_{BX} = 1.4$ c.p.s.). The two bridgehead protons D and C lie at 190 and 178 c.p.s., respectively. Although they are partially merged at 60
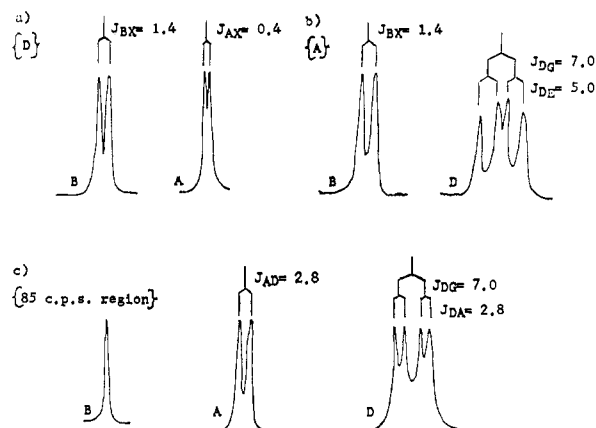
Mc., they are quite distinct at 100 Mc. The triplet (or latent quartet) exhibited by D is due to its coupling with only G and E. A consideration of the appropriate dihedral angles in a Dreiding model of VII, shows that J_{DF} and J_{DH} will be negligibly small and that J_{DE} and J_{DG} correspond to 4.0 and 6.0 c.p.s., respectively. The other bridgehead proton C merely shows as an unresolved hump as C couples with protons B, E, and I. The methylene protons show as a wide multiplet centered at 113 c.p.s.

Figure 4 depicts the changes which the signals of B, D, and C undergo in different decoupling experiments.

Irradiation of the bridgehead proton C merely collapses the vinyl resonance to a thinly spaced doublet ($J_{BX} = 1.4$ c.p.s.) (Figure 4a).

Conversely, irradiation of the vinyl proton B transforms the hump of proton C to a triplet (latent quartet) with spacings of 2.0 and 4.0 c.p.s. These two values most probably correspond to J_{CE} and J_{CI}. Meanwhile, the triplet of bridgehead proton D remains intact (Figure 4b).

Observation of the spectrum of VII is particularly instructive when the methylene region is irradiated. Irradiation of the central region (at 115 c.p.s. from TMS on the 60-Mc. spectrum) causes both bridgehead proton signals to collapse. D becomes a doublet spaced at 4.0 c.p.s. C becomes a blunt doublet spaced at 7.0 c.p.s., with each peak about 2.0 c.p.s. wide, (Figure 4c). This simplification is undoubtedly due to the decoupling of I and G, and it is significant that the vinyl signal is unaffected. Clearly, protons I and G cannot be X.

Irradiation in the upfield portion of the methylene region (at 96 c.p.s. from TMS on the 60-Mc. spectrum) is critical. The vinyl signal becomes a wide doublet of 7.0 c.p.s. The bridgehead protons respond differently; C remains as a broad hump, whereas D shows as a widely spaced doublet of 6.0 c.p.s. (Figure 4d). These simultaneous changes reinforce the previous deduction that protons E and X are one and the same.

Discussion

It is significant that protons E and A are situated on the terminal limbs of a W arrangement of σ-bonds, which has been shown previously to be a stereochemical requirement for long-range coupling.[13-17]

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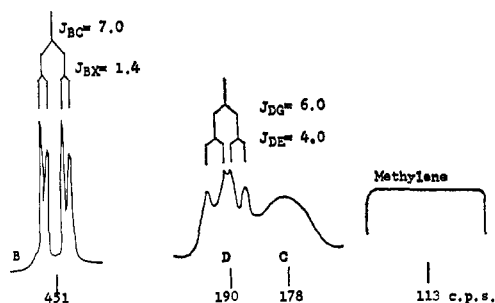Figure 3. The 60-Mc. spectrum of VII in CCl₄ solution.

Figure 4. Signal simplification of VII during irradiation.

Moreover, proton E bears a special relationship to the vinyl proton B. From a Dreiding model it can be seen that the small backside lobe of the sp³ orbital of the C-8-E bond can overlap reasonably well with both p-orbitals of the double bond and thus affords a coupling mechanism. Such an interaction has been used to explain the enhanced solvolytic activity of *anti*-8-bicyclo[3.2.1]oct-2-enyl tosylate (compared with its *syn* isomer).[18] Furthermore, the same argument has been invoked in similar circumstances for 7-substituted norbornenyl derivatives.[19,20]

The rigid bicyclo[3.2.1]octene-2 (VIII) framework is unique in that three kinds of long-range coupling (W plan, homoallylic, and allylic) are geometrically possible. An explanation for the absence of conventional allylic coupling in compounds IV–VI may be found in terms of the reflex effect.[16,21,22] The formation of VIII by the
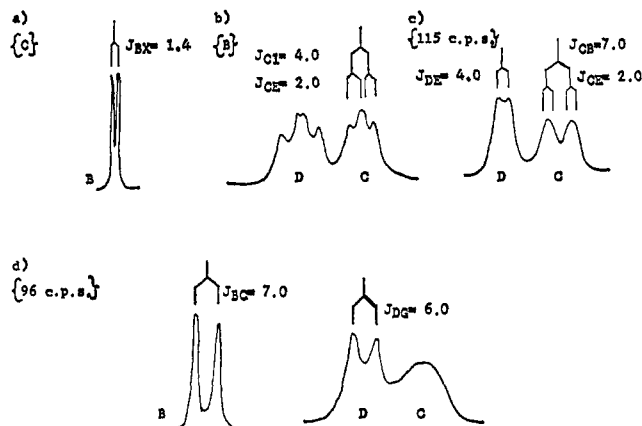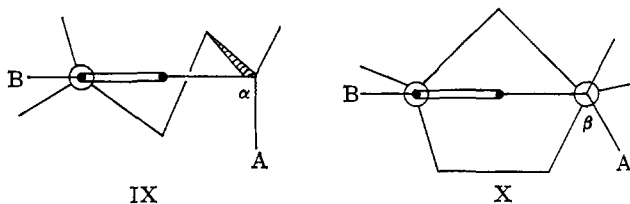

IX   X

attachment of the ethane bridge to the cyclohexene moiety flattens its usual half-chair conformation. Comparison of the Newman projections IX and X reveals that the result of the distortion is to increase the angle between the allylic bond and the plane of the double bond; $\beta > \alpha$, which may decrease the σ–π orbital contact and minimize allylic coupling.

Experimental

The preparation of the bicyclo[3.2.1]octene-2 derivatives IV–VII is described in a previous paper.

N.m.r. Spectra. Spectra were determined at 60 and 100 Mc. on Models A-60 and HR-100 spectrometers (Varian Associates, Palo Alto, Calif.) at magnet temperatures of 25 and 30°, respectively. Compounds were studied in approximately 10% solutions of carbon tetrachloride. Chemical shifts were measured in cycles per second (c.p.s.) from tetramethylsilane (TMS) as internal standard and are considered accurate to ± 1.0 c.p.s. Coupling constants (J) are also expressed in c.p.s. and considered accurate to ± 0.1 c.p.s. Line positions at 100 Mc. were obtained by audiomodulation of the magnetic field.

A Hewlett–Packard audiofrequency oscillator (200 J) and counter (5512 A) were used. The decoupling experiment was performed with a Varian integrator utilizing the field-sweep technique.[23] The precise positions of maximum decoupling were found by plotting the frequency of the audiofrequency signal used to generate the decoupling side band against peak height of the observed signal by the procedure of Freeman.[24]

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