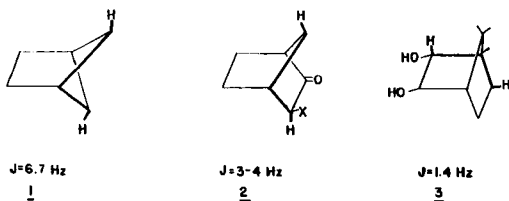# Long-Range Spin-Spin Coupling in Bicyclo[3.1.0]hexane Systems

By ROGER C. BRIDEN, EDWARD E. SMISSMAN*, and MARY WEIR CREESE

The NMR parameters of 3-bromo-bicyclo[3.1.0]hexan-4-one-1-carboxylic acid ethylene ketal and ethyl bicyclo[3.1.0]hex-2-ene-4-one-1-carboxylate have been recorded and the chemical shifts of all protons assigned. Both of these compounds show interesting cases of long-range spin-spin coupling.

L ONG-RANGE ^{1}H-^{1}H spin-spin coupling in general (1, 2), and coupling through 4-σ bonds in particular (3–6), are receiving increasing attention. Two features are apparent in compounds exhibiting 4-σ bond coupling: first, the compounds have well-defined stereochemistry resulting from the rigidity of the molecule due to a fixed or preferred conformation; second, the H—C—C—C—H skeleton through which protons are coupled exists in a $\bigvee\bigwedge\diagup$ configuration.

The magnitudes of the coupling constants reported for 4-σ bond coupling range from less than 1 to about 7 c.p.s., with values of 1–2 c.p.s. being most common. Some examples of compounds in which long-range 4-σ bond coupling has been observed are shown by *1, 2,* and *3* (4–6).

coupling in 3-bromo-bicyclo[3.1.0]hexan-4-one-1-carboxylic acid ethylene ketal (*4*) and in ethyl bicyclo[3.1.0]hex-2-ene-4-one-1-carboxylate (*5*).

4   **5**
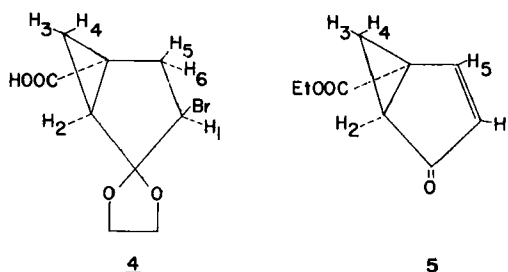
The 100-Mc.p.s. spectrum of *4* is shown in Fig. 1. The coupling constants and chemical shift values determined from this spectrum are listed in Table I.

RESULTS AND DISCUSSION

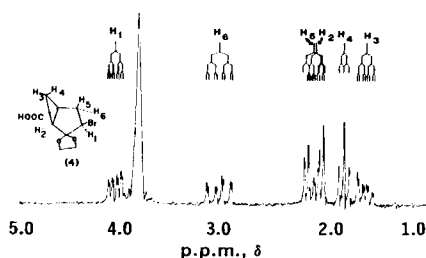The ethylene ketal resonance is assigned to the 3.88-δ absorption on the basis of its four-proton

J=6.7 Hz   J=3-4 Hz   J=1.4 Hz

1   *2*   *3*

The authors have observed long-range 4-σ bond

Fig. 1—100-Mc.p.s. spectrum of 4.

TABLE I—NMR PARAMETERS

Compd.	H-1	H-2	H-3	H-4	H-5	H-6
			Proton Chemical Shifts, δ			
4	4.08	2.10	1.57	1.79	2.15	3.07
5	5.67	2.76	2.17	1.82	7.87	

	Geminal		Vicinal		Long-Range	
		Coupling Constants, c.p.s.				
4	J-34 = 5.5		J-15 = 4.0		J-12 = 1.5	
	J-56 = 15.0		J-16 = 8.5		J-36 = 1.5	
			J-23 = 9.5			
			J-24 = 5.5			
5	J-43 = 3.0		J-15 = 5.5		J-12 = 1.0	
			J-24 = 4.5			
			J-23 = 8.5			

integration and its field position. The 4.08-δ absorption is assigned to H-1 as this proton is on a bromine-bearing carbon and thus will absorb furthest downfield. H-1 is coupled to three other protons with coupling constants of 8.5, 4.0, and 1.5 c.p.s. The dihedral angle between H-1 and H-6 is 0°, while that between H-1 and H-5 is 120°. The modified Karplus plot allows the predication that J-16 should be about 10 c.p.s. and J-15 about 4 c.p.s. (7). Therefore, the observed coupling constants 8.5 and 4.0 c.p.s. have been assigned as J-16 and J-15, respectively. The 1.5-c.p.s. splitting is assigned to long-range coupling between H-1 and H-2 based on the magnitude of the coupling, the observed \/\/ configuration of the H$_1$—C—C—C—H$_2$ system, and the absence of another proton in the molecule to which this coupling can reasonably be assigned. Double resonance experiments (Figs. 2b and 3b) indicate that the proton (H-2) which is responsible for this 1.5-c.p.s. splitting lies in the upfield portion of the 2.1-δ multiplet. The lack of clean decoupling for protons H-1 and H-6 when irradiating H2 (Fig. 2b) may be attributed to the proximity of the H-5 resonance to the point of irradiation and possibly to virtual spin-spin decoupling of H-6 through H-1.

The proton resonance at 3.07 δ is coupled to three other protons with J values of 15.0, 8.5, and 1.5 c.p.s. Proton H-6 is assigned to this absorption because of the observed 8.5-c.p.s. coupling between H-1 and H-6. The 15.0-c.p.s. coupling is reasonable for geminal coupling (8) and is probably negative in sign. This coupling is assigned as J-65. The remaining 1.5 c.p.s. coupling can be assigned to long-range coupling between H-6 and either H-2 or H-3 as both 5-atom systems exist in a \/\/ configuration. Double-resonance experiments (Figs. 2a and 3a) show that this 1.5-c.p.s. splitting results from coupling to the proton absorbing at 1.6 δ. As double resonance techniques have indicated that H-2 absorbs in the 2.1-δ region, this 1.5-c.p.s.

coupling and the 1.6-δ absorption are assigned to H-3.

Proton H-3 is coupled to three other protons with coupling constants of 9.5, 5.5, and 1.5 c.p.s. The 1.5-c.p.s. splitting has been assigned as J-36. The J values of 9.5 c.p.s. and 5.5 c.p.s. agree with those reported for *cis* and geminal coupling on cyclopropane rings (8). These couplings are assigned as J-32 = 9.5 c.p.s. and J-34 = 5.5 c.p.s.

The 2.1-δ resonance can be divided into two parts: one part shows coupling to two other protons with J values of 15.0 c.p.s. and 4.0 c.p.s. Proton H-5 is assigned to this part because of its 15.0-c.p.s. coupling to H-6. The coupling constants are assigned as J-56 = 15.0 c.p.s. and J-51 = 4.0 c.p.s.

Because of its 9.5-c.p.s. coupling constant and double resonance experiments, the second part of the 2.1-δ multiplet is assigned to H-2. The observed coupling constants of 9.5, 5.5, and 1.5 c.p.s. are assigned as J-23 = 9.5 c.p.s., J-24 = 5.5 c.p.s., and J-21 = 1.5 c.p.s.

The final multiplet in the spectrum at 1.79 δ is assigned to H-4. The coupling constants are assigned as J-43 = 5.5 c.p.s. and J-42 = 5.5 c.p.s.

The 60-Mc.p.s. spectrum of *5* is shown in Fig. 4, and the chemical shifts and coupling constants are listed in Table I. The one-proton doublet at 7.87 δ is assigned to H-5 because the β-olefinic proton of an α,β-unsaturated ketone, cyclic or acyclic, usually lies further downfield than the α-olefinic proton (9).
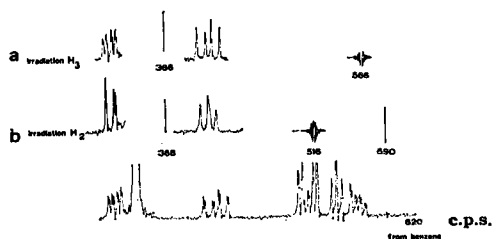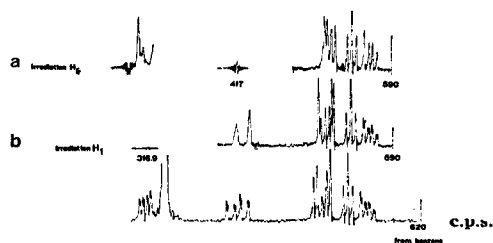
Fig. 3—100-Mc.p.s. spectrum of 4.

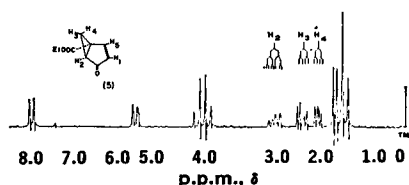*Fig. 4—60-Mc.p.s. spectrum of* 5.

Fig. 2—100-Mc.p.s. spectrum of 4.

The 5.5-c.p.s. splitting is due to vicinal coupling of H-5 with H-1. Proton H-1 is assigned to the 5.67-δ doublet which is further split. The 5.5-c.p.s. coupling of this doublet of doublets is due to H-5, H-1 coupling while the 1.0-c.p.s. splitting is assigned to the long-range coupling of H-1 with H-2. The broad doublet of doublets at 2.76 is assigned to H-2, the 8.5-c.p.s. splitting being due to coupling between H-2 and H-3 which are *cis* to one another. The coupling between the *trans* protons H-4 and H-2 is assigned to the 4.5-c.p.s. splitting and the broadening of each peak to the long-range coupling of H-2 to H-1. The two remaining one-proton multiplets at 2.17 δ and 1.82 δ are assigned to H-3 and H-4, respectively. H-3 is coupled to H-2 by 8.5 c.p.s. and to H-4 by 3.0 c.p.s. H-4 is in like manner coupled to H-2 by 4.5 c.p.s. and to H-3 by 3.0 c.p.s. The triplet at 1.30 δ and the quartet at 4.18 δ are obviously due to the ethyl group of the ester. The 1.49-δ singlet is due to a *tert*-butyl group resonance, the *tert*-butyl ester having been formed by transesterification during the synthesis of *5* (10).

The magnitudes of the vicinal coupling constants observed in these systems are in agreement with values reported previously for some substituted cyclopropanes by Graham and Rogers (8). In these systems they found that *J-cis* ranged from 7.90 to 9.33 c.p.s. and averaged 8.44 c.p.s. and that *J-trans* ranged from 5.28 to 6.55 c.p.s and averaged 5.68 c.p.s. The geminal coupling constant varied over a large range but the sum of *J-cis* + *J-trans* + *J-gem* was virtually constant at 20.68 to 21.61 c.p.s. The coupling constants observed for Compound *4* are *J-cis* = 9.5, *J-trans* = 5.5, and *J-gem* = 5.5 c.p.s., giving a sum of 20.5 c.p.s., which is near the reported range, thus suggesting that the cyclopropane system in this bicyclo compound is near normal. In Compound *5* the analogous coupling constants are 8.5, 4.5, and 3.0 c.p.s., respectively, giving a sum of 16 c.p.s. which is significantly below the reported range. The low value of the geminal coupling constant (*J*-34) is of particular interest and probably results from a combination of effects among which should be included the sensitivity of geminal coupling to the H—C—H bond angle and the substituent effects of the carbonyl and the double bond.

Long-range coupling in Compound *4* occurs between protons H-1 and H-2, and between H-6 and H-3. No coupling is observed between H-6 and H-2. The ∨∕∨ between H-1 and H-2 is similar but more planar than that formed between H-2 and H-6. This, plus substituent effects (3, 11) may account for the absence of coupling between H-2

and H-6. Compound *5* shows only one case of long-range coupling, that between H-1 and H-2. Although the lack of long-range coupling between H-5 and H-3 presumably results from a combination of a substituent and a steric effect caused by the introduction of the double bond, other effects are not ruled out. The absence of long-range coupling between H-5 and H-3 is clear from the half-band width of the H-3 resonance which is, within experimental error, the same as that of the TMS resonance and the methylene quartet of the ethyl ester group.

This bicyclo[3.1.0]hexane system (*4*), which provides an example of relatively rare long-range coupling of cyclopropane hydrogens through 4-σ bonds, also illustrates the utility of the commonly observed ∨∕∨ configuration in long-range spin-spin coupling in assigning chemical shifts of closely related protons in such systems.

EXPERIMENTAL

The proton resonance spectra were obtained on Varian A-60 and HA-100 high-resolution NMR spectrometers. Chemical shifts are reported in δ. The 100-Mc.p.s. spectra were observed using benzene as the lock signal. Each sample was run as a 10–15% solution in deuterochloroform containing TMS as the internal reference.

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⊙⟶ *Keyphrases*

Bicyclo[3.1.0]hexane systems

Spin-spin coupling, long-range—bicyclo [3.1.0]hexane systems

Coupling constants—bicyclo[3.1.0]hexane systems

NMR spectroscopy—chemical shifts