Bridged Polycyclic Compounds. XXVIII. The Proton Magnetic Resonance Spectra of Some Dibenzobicyclo[3.2.1]octadienes[1]

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P.m.r. spectra for a number of 4- and 8-substituted dibenzobicyclo[3.2.1]octadienes have been measured. Correlations of these data lead to generalizations which permit stereochemical assignments for substituents in these systems.

The p.m.r. spectra discussed here were obtained in the course of elucidating the stereochemical consequences of some carbonium ion reactions in derivatives of dibenzobicyclo[3.2.1]octadiene.[2,3] During this work a large number of mono- and disubstituted dibenzobicyclo[3.2.1]octadienes with known stereochemical configuration became available. Examination of the spectra led to a useful correlation by which compounds in this series can be assigned known stereochemical configurations.

The structures and configurations of many of the compounds listed in Table I have been proved in this laboratory by chemical[2-4] and dipole moment[5] studies. The remaining compounds will be described in detail in later papers. A preliminary account of some of the interesting carbonium ion pathways and stereochemical consequences of these reactions has already appeared.[2]

All spectra were obtained using a Varian A-60 n.m.r. instrument. The spectra were taken in carbon tetrachloride solution, except that in a few cases that are noted deuteriochloroform was used for solubility reasons. In general, saturated solutions of the compounds studied were used. The spectra were swept over a range of τ 2–10 using tetramethylsilane (τ = 10) as an internal standard.

It was possible to assign spectral frequencies to each of the four aliphatic protons in the 4,8-disubstituted dibenzobicyclo[3.2.1]octadienes (for numbering see Figure 1) herein reported because their chemical shifts were generally different enough to give separate peaks for each proton. An illustration of the basis for these spectral assignments can be found in the proton assignments in the n.m.r. spectrum of *exo*-4-acetoxy-*syn*-8-chlorodibenzobicyclo[3.2.1]octadiene. This spectrum has a total of five absorption peaks corresponding to the five different classes of aliphatic protons bound to carbon. The five absorptions present at τ 4.33, 5.30, 6.03, 6.37, and 7.90, show relative areas of 1:1:1:1:3, where the aromatic protons integrate to a relative area of 8.[6] We can immediately assign the τ 7.90 absorption to the three identical protons α to the carbonyl group of the acetate function. The four remaining protons then must be those bound to carbon at the 1-, 4-, 5-, and 8-positions. From the correlation of all of the n.m.r. spectra of disubstituted compounds related to I in Table I it is apparent that the absorption peaks at τ 6.03 and 6.37 can be assigned to the two bridgehead protons attached to carbons 1 and 5. This is consistent with the assignment of the absorption peak at τ 5.81 in dibenzobicyclo[2.2.2]octadiene to the two bridgehead protons. The τ 5.81 peak is the lowest aliphatic peak and appears at a frequency consistent with the deshielding effect of two α-benzene rings. Thus the α-protons in ethylbenzene are at τ 7.38[7] while those of diphenylmethane are at 6.08.[7] By this reasoning the τ 6.03 peak was assigned to the proton on C-1, which is α to two benzene rings, and the 6.37 τ peak was assigned to the proton at C-5, which is α to only one benzene ring. The absorption peak at τ 4.33 has been assigned to the proton at C-4, since here both the effect of the α-benzene ring and the α-acetoxy group reinforce each other to produce a large chemical shift. The remaining absorption at τ 5.30 has been assigned to the proton on C-8, α to the chlorine atom. In analogy to this it has been observed that isopropyl chloride has an absorption peak at τ 5.87 assigned to the proton α to the chlorine.[7]

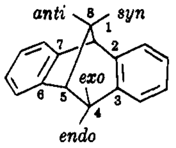

Figure 1.—The dibenzobicylo[3.2.1]octadiene ring system.

Further evidence for proton assignments is found in observing the effects of substitution upon the position of spectral lines. For example, the only large differences in the position of peaks in *exo*- and *endo*-4-acetoxy-*syn*-8-chlorodibenzobicyclo[3.2.1]octadiene (compounds **1** and **3**, Table I, respectively) is in the position of the resonance assigned to the proton α to the acetoxy group. On the other hand, in the corresponding *anti* series (compounds **2** and **4**, Table I), the chemical shifts assigned to the protons on both C-4 and C-8 are significantly different in the *endo* and *exo* series. In the *syn*-8-chloro compounds, the proton at C-4 finds itself in considerably different environments depending upon whether it is *exo* or *endo*, while the *anti*-8-proton is not affected by changes at C-4. However, for the *syn*-8-proton, the environment changes substantially depend-

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[1] Previous paper in series: S. J. Cristol, T. W. Russell, and D. I. Davies, *J. Org. Chem.*, **30**, 207 (1965).

[2] (a) S. J. Cristol, J. R. Mohrig, F. P. Parungo, D. E. Plorde, and K. Schwarzenbach, *J. Am. Chem. Soc.*, **85**, 2675 (1963); (b) S. J. Cristol, Abstracts of the Eighteenth National Organic Symposium of the American Chemical Society, Columbus, Ohio, 1963, p. 12.

[3] (a) S. J. Cristol, R. P. Arganbright, and D. D. Tanner, *J. Org. Chem.*, **28**, 1374 (1963); (b) S. J. Cristol and D. D. Tanner, *J. Am. Chem. Soc.*, **86**, 3122 (1964).

[4] S. J. Cristol and R. K. Bly, *ibid.*, **82**, 6155 (1960).

[5] D. D. Tanner and T. S. Gilman, *ibid.*, **85**, 2892 (1963).

[6] In all n.m.r. spectra considered here the large peak assigned to the aromatic protons at approximately τ 2.9 was used only for the determination of relative peak areas. The significance of the complex splitting pattern and the minor changes in the chemical shifts of these protons was not considered in detail.

[7] G. V. D. Tiers, "Characteristic Nuclear Magnetic Resonance 'Shielding' Values (Spectral Positions) for Hydrogen in Organic Structures," Central Research Department, Minnesota Mining and Manufacturing Co., Inc., St. Paul, Minn., March 28, 1958.

TABLE I
PROTON ASSIGNMENT IN THE DIBENZOBICYCLO[3.2.1]OCTADIENE SYSTEM I

No.	Compd.	Chemical shift, τ *exo*-4-H	 *endo*-4-H	 *syn*-8-H	 *anti*-8-H	 5-H	 1-H	 Other	J, c.p.s.
1	*exo*-4-Acetoxy-*syn*-8-chloro I		4.33		5.30	6.37	6.03	7.90 (acetate)	$J_{45} = 1.5$ $J_{18} = J_{58} = 4.3$
2	*exo*-4-Acetoxy-*anti*-8-chloro I		4.07	5.10		6.36	5.93	7.97 (acetate)	$J_{45} = 2.4$ J_{18} = very small
3	*endo*-4-Acetoxy-*syn*-8-chloro I	3.84			5.31	6.30	6.12	8.01 (acetate)	$J_{45} = 5.4$ $J_{18} = 4.5$
4	*endo*-4-Acetoxy-*anti*-8-chloro I	3.84		5.44		6.02	5.97	7.97 (acetate)	$J_{45} = 5.5$ $J_{18} = \sim 0.5$
5	*exo*-4-*syn*-8-Dichloro I		5.12		5.36	6.31	6.10		$J_{45} = <1$ $J_{18} = 4.4$
6	*endo*-4-*syn*-8-Dichloro I	4.36			5.23	6.36	6.09		$J_{45} = 4.8$ $J_{18} = 4.3$
7	*exo*-4-*anti*-8-Dichloro I		4.87	4.87		6.15	5.95		J_{45} = ? J_{18} = very small
8	4-Keto-*syn*-8-chloro I				4.97	5.83	6.02		$J_{18} = 4.5$
9	4-Keto-*anti*-8-chloro I			5.07		5.68	5.82		$J_{18} = <1$
10	*exo*-4-*syn*-8-Diacetoxy I		4.26		4.68	6.15	6.01	7.94 8.12 (acetates)	$J_{45} = 1.5$ $J_{18} = 5.0$
11	*exo*-4-Acetoxy-*syn*-8-chloro I ($CDCl_3$ solvent)		4.22		5.23	6.30	5.95	7.86 (acetate)	$J_{45} = 1.4$ $J_{18} = 4.3$
12	*exo*-4-Acetoxy I		4.27	7.59[a]		6.55	6.16	7.97 (acetate)	$J_{45} = 2.5$ $J_{18} = 3.0$
13	*endo*-4-Acetoxy I	3.87		7.63	7.47	6.25		7.97 (acetate)	$J_{45} = 5.5$ $J_{18} = 4.5$
14	*exo*-4-Hydroxy I		5.60	7.65[a]		6.69	6.22	6.69 (alcohol)	$J_{18} = 2.5$
15	4-Keto I			7.33	7.29	5.97	6.12		$J_{18} = 3.8$
16	*exo*-4-Chloro I		4.99	7.38	7.46	6.34	6.17		$J_{45} = 1.8$ $J_{18} = 4.0, 1.1$
17	*syn*-8-Chloro I				5.32		6.10		$J_{18} = 4.5$
18	*exo*-4-Acetoxy-*anti*-8-nitro I ($CDCl_3$ solvent)		3.88	4.73		5.68	5.20	7.82 (acetate)	$J_{45} = 2.6$ $J_{18} = 0.8$
19	*exo*-4-Hydroxy-*anti*-8-nitro I ($CDCl_3$ solvent)		5.07	4.75		5.74	5.27	7.76 (alcohol)	$J_{45} = 2.3$ J_{18} = very small
20	4-Keto-*anti*-8-nitro I			4.81		5.03	5.25		$J_{18} = 0.8$
21	*exo*-4-Hydroxy-*syn*-8-amino I ($CDCl_3$ solvent)		5.44		5.86	6.50	6.12	7.16 (combined alcohol and amine)	J_{45} = ? $J_{18} = 4.5$
22	*anti*-8-Chloro I	6.72	7.07	5.42		6.43	6.00		$J_{45} = 4.5$ J_{18} = very small
23	*exo*-4-Acetoxy-*syn*-8-bromo I		4.36		5.23	6.33	5.97	7.86 (acetate)	$J_{45} = 1.6$ $J_{18} = 4.3$
24	*endo*-4-Acetoxy-*syn*-8-bromo I	3.72			5.17	6.39	6.02	7.93 (acetate)	$J_{45} = 5.5$ $J_{18} = 4.0$
25	*exo*-4-Acetoxy-*syn*-8-iodo I		4.47		5.31	6.39	6.06	7.90 (acetate)	$J_{40} = 1.0$ $J_{18} = 3.5$
26	*exo*-4-*anti*-8-Diacetoxy I		4.12	4.43		6.45	5.97	7.88 8.10 (acetates)	$J_{45} = 2.0$ $J_{18} = 1.0$
27	Hydrocarbon I	6.98	7.27	7.90	7.61	6.66	6.24		$J_{45} = 4.5$ $J_{18} = 4.0$

[a] These two hydrogen resonances appeared at almost identical positions. The multiplets appeared to be the sums of triplets for the *anti* protons with the coupling constants noted and triplets with rather negligible coupling constants which thus appeared to be singlets.

ing upon whether a proton or an acetoxy group is *exo* at C-4. Similarly *exo*- and *endo*-4-*syn*-8-dichloro I (compounds **5** and **6**, Table I) differ significantly in only one peak. This is assigned in each case to the 4-proton since it is observed at the lowest field of all of the aliphatic protons (this proton experiences deshielding by both an α-chlorine and an α-benzene ring). It should be noted that the *anti*-8-protons in the above-mentioned compounds **1**, **3**, **5**, and **6**, Table I, possess almost the same chemical shift (τ 5.30, 5.31, 5.36, and 5.23) regardless of the different substitution involved at C-4.

Similar factors have been considered in the proton assignments in all of the compounds listed in Table I. No significant anomalies have been encountered in the assignments of chemical shifts in the compounds listed. Approximate chemical shifts are noted whenever possible in these spectra. When approximate numbers are used, they are always noted as being such.

The results obtained for the spin–spin coupling constants for the proton attached to the methylene bridge carbon (C-8) of a substituted dibenzobicyclo[3.2.1]octadiene are found in Table II. Only vicinal couplings are considered here. High-resolution spectra showed small splittings undoubtedly due to long-range interactions. No attempt was made to interpret these couplings. An example is the spectrum of *exo*-4-acetoxy-*syn*-8-chlorodibenzobicyclo[3.2.1]octadiene. In this spectrum the

TABLE II

AVERAGE VALUES FOR COUPLING CONSTANTS FOR 4- AND 8-SUBSTITUTED DIBENZOBICYCLO[3.2.1]OCTADIENE[a]

Compd. series	No. of examples	Spin–spin coupling constants, J (c.p.s.)
exo-4-Substituted (*endo*-4-proton)	12	$J_{45} = 1.8 \pm 0.5$
endo-4-Substituted (*exo*-4-proton)	7	$J_{45} = 5.1 \pm 0.5$
syn-8-Substituted (*anti*-8-proton)	14	$J_{18} = J_{58} = 4.2 \pm 1.0$
anti-8-Substituted (*syn*-8-proton)	9	$J_{18} = J_{58} = <1$

[a] Limits of error are *standard deviations.*

τ 4.33 absorption assigned to the 4-proton is a doublet with a splitting of 1.5 c.p.s. The τ 6.03 and 6.37 peaks are both doublets with a 4.3 c.p.s. splitting. In addition the doublet at τ 6.37 assigned to the 5-proton is partially split again, but the further splitting is small, and the peaks are not well resolved. The τ 6.03 peak is a very sharp doublet. The τ 5.30 absorption assigned to the 8-proton is a triplet with a 4.3 c.p.s. coupling constant. This is as expected, since the coupling of the 8-proton with both of the bridgehead protons would be expected to be the same, as the dihedral angle is the same for both pairs of protons. Thorough study of the spectra listed has shown that the absorption peak assigned to the 4-proton, which is a doublet whose splitting varies, has a coupling constant which can always be accommodated in the multiplet assigned to the 5-proton. Furthermore the splitting constant noted in the absorption peak assigned to the 8-proton is invariably reflected in the multiplets assigned the 1- and 5-protons. The peak assigned to the 5-proton is sometimes poorly resolved due to the additional coupling with the 4-proton.

The stereochemical configuration of a 4,8-disubstituted dibenzobicyclo[3.2.1]octadiene can therefore readily be determined by a study of its n.m.r. spectrum through the consideration of two factors.

The absorption peak assigned to the 8-proton is a distinct triplet in *syn*-substituted compounds (where the 8-proton has the *anti* configuration), with coupling constants between that proton and the 1- and 5-bridgehead protons ($J_{18} = J_{58}$) of about 4 to 5 c.p.s. On the other hand, in the *anti*-8-substituted compounds, coupling constants observed between the *syn*-8-proton and the bridgehead protons ($J_{18} = J_{58}$) are less than 1.0 c.p.s., so that the *syn*-8-proton peak is either a singlet or a closely spaced triplet. The absorption peak assigned to the 4-proton is a doublet in which the coupling constant is small (approximately 2 c.p.s.) in an *exo*-4-substituted compound (*endo*-4-proton) and large (approximately 5 c.p.s.) in an *endo*-4-substituted compound. No exceptions to these relationships between stereochemical configuration in this system and corresponding n.m.r. spectral pattern have been observed in this laboratory.

If one takes the data of Table II and assigns dihedral angles with a plot[8] according to the method of Karplus,[9] with respect to the bridgehead proton on C-5, such dihedral angles are: the *endo*-4-proton, 60°; the *exo*-4-proton, 40°; the *anti*-8-proton, 40°; and the *syn*-8-proton, 80°. Allowing for the fact that the sum of dihedral angles of the first pair should be 120° rather than 100°, these angles are not inconsistent with those measured from a model (Dreiding molecular models), although distortions in the model due to angle strains are not readily accommodated in this system. These data do, however, provide further evidence that two vicinal protons having a dihedral angle near 0° show large coupling constants and those having a dihedral angle near 90° exhibit small coupling constants.

One might expect to find similar coupling patterns in simple bicyclo[3.2.1]octane derivatives as well. Analogous results have been reported[10] for several such cases.

It is of interest that an *endo*-4-proton absorbs at a higher field than the epimeric *exo*-4-proton by τ 0.2–0.8. This has been observed previously in bicyclo[2.2.1]heptanes.[8,11,12] Unfortunately both of a pair of compounds epimeric at the 4-position must be studied to determine the structure of each using this correlation, since small changes in chemical shifts occur frequently and unpredictably among analogous compounds.

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