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NMR STUDIES OF BRIDGED RING SYSTEMS. X.*[1]

LONG-RANGE ANISOTROPIC SHIELDING EFFECTS OF AN EPOXIDE AND AN AZIRIDINE RING

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WHILE some doubts have recently been aroused (1) upon the NMR signals of the bridge C-7 syn- and anti-protons in norbornene (II) and benzonorbornene (III) assigned by us (2), we have reported in a previous communication that the reversals of our previous assignments in the syn- and anti-proton signals have been confirmed by using proton spin-decoupling and deuteration methods (3). Thus, it became highly necessary to confirm assignments of the bridge proton signals of their epoxide and aziridine derivatives reported earlier (4, 5) and also to revise the long-range anisotropic shielding values exerted by an epoxide and an aziridine ring introduced into II and III (5).

In order to remove all questions as to the assignments leading to the estimation of magnitude of the long-range anisotropic shielding effects of a three-membered ring, which are in principal summarized as that a proton situated above the plain of the ring is more shielded, whereas a proton located near in the plain of the ring or in the neighborhood of the heteroatom in the ring is less shielded (5, 6), we firstly

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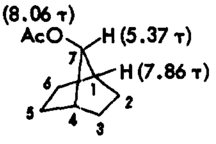
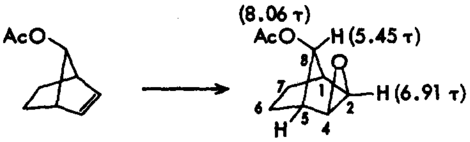
*[1] For Part IX, see Ref. (3).

synthesized *anti*-8-acetoxy-3-oxa-tricyclo[3.2.1.0^{2,4}-*exo*]octane (VIII) by epoxidation of *anti*-7-acetoxynorbornene (VII) and compared the NMR spectrum of VIII with that of 7-acetoxynorbornane (VI).[*2,*3] Introduction of an epoxide ring into VI causes only 0.08 p.p.m. of an upfield shift to the C-7 proton signal in VI. This fact indicates that the C-8 *syn* proton in VIII located within the much shielding zone of the epoxide ring , is less shielded owing to the proximity of the oxygen atom, and accordingly, that the doublet signals at higher fields in the compounds XI-XIII (see TABLE II) (4, 5) were conclusively proved to arise from the C-8 *anti* protons.

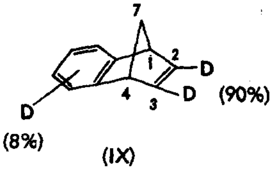


(VI)



(VII) (VIII)

Secondly, we confirmed the presence of long-range spin-coupling between the C-2 (C-4) protons and the C-8 proton *anti* to them by using proton spin-decoupling experiments on the compound XIII (Y=O) and further by examining the spectrum of 2,4-dideutero-3-oxo-5,6-benzotricyclo[3.2.1.0^{2,4}-*exo*]octene (X) prepared from 2,3-dideuterobenzonorbornadiene (IX) (3, 7)(see FIG. 1). Similarly, spin-decoupling experiments at 100 Mc.p.s. field on the compounds XII, XIII (Y=NH), and XIV (Y=O, NH) revealed the assignments of their bridge proton signals by the presence of long-range spin-couplings between the C-2 (C-4) protons and the C-8 proton *anti* to them.



(IX)

[*2] NMR spectra were taken with a Varian HA-100 spectrometer operating at 100 Mc.p.s. field in the frequency sweep and TMS-locked mode, by using about 5% (w/v) solutions in carbon tetrachloride containing about 1% TMS as an internal standard.

[*3] The numbering of the skeletal carbons used in this paper is conventional, and *syn* and *anti* in II-IV are prefixed towards the π-systems, but in VIII-XV towards the three-membered rings.

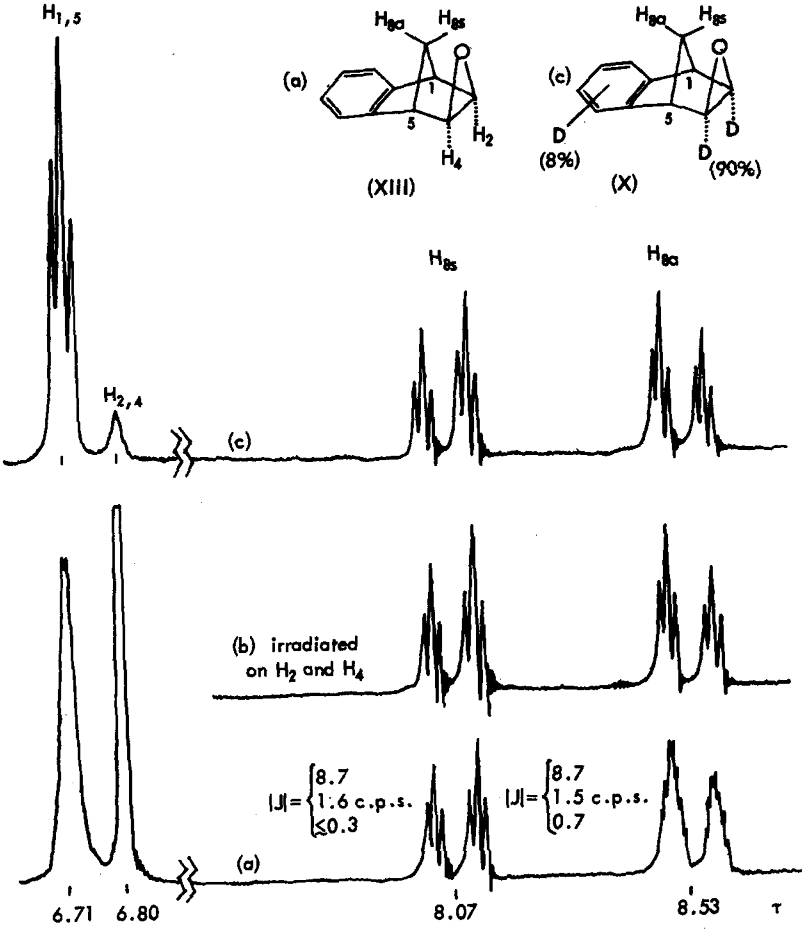
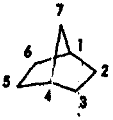
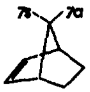
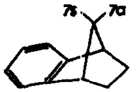
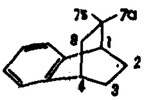
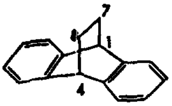


FIG. 1 NMR spectra of XIII (Y=O)(a and b) and X (c) in CCl_4 at 100 Mc.p.s. Lower field parts of the spectra are not shown.

TABLE I

NMR Data on Parent Compounds Examined in Carbon Tetrachloride

Compound		Chemical shift (τ)				Ref.
		Bridgehead C-1, C-4 protons	Bridge C-7s protons	Bridge C-7a protons	Olefinic protons	
	(I)	7.80 7.81	8.79 8.74		–	(3) (8)
	(II)	7.17 7.22	8.68	8.93	4.07 4.06	(3) (8)
	(III)	6.70	8.27	8.52	–	(3)
	(IV)	7.06	~8.61	~8.25	–	This work (5)
	(V)	5.77	8.32		–	This work

In TABLE I are shown the chemical shifts of protons in the parent compounds examined, and the anisotropic shielding effects (additional shift values) due to introduction of an aziridine or an epoxide ring into these parent compounds are listed in TABLE II, which involves some revisions of the data earlier reported (5) and some new data.*4 The anisotropic shielding values obtained from the norbornene derivatives, XI, XII, and XIII, are different in signs and magnitudes, particularly for the

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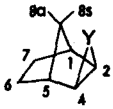
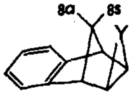
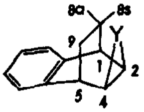
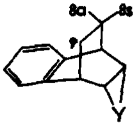
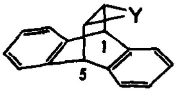
*4 Evidence for the long-range anisotropic shielding effects characteristic of these three-membered rings was presented in a previous paper (5).

TABLE II

Anisotropic Shielding Effects Due to an Aziridine and an Epoxide Ring in Carbon Tetrachloride

Compound		Y	Additional shift value (p.p.m.)[a] Bridgehead C-1, C-5 protons	Bridge C-8a	C-8s protons	Olefinic protons	Ref.
	(XI)	NH	-0.09	+0.68	~+0.04	-	(5)
		O	-0.21	+0.63	-0.06	-	(5)
	(XII)	NH	+0.08	+0.37	-0.49	-0.36	This work
		O	-0.06	+0.12	-0.49	-0.45	This work[b]
	(XIII)	NH	+0.12	+0.46	-0.45	-	This work
		O	-0.01	+0.26	-0.45	-	This work
	(XIV)	NH	-0.21	~+0.38	~-0.23	-	(5)
		O	-0.28	~+0.37	~-0.28	-	(5)
	(XV)	NH	-0.39	~+0.01	~ 0.00	-	(5)
		O	-0.41	~+0.05	~+0.03	-	(5)
	(XVI)	NH[c]	-0.14	-	-	-	This work
		O [d]	-0.22	-	-	-	This work

[a] Plus sign represents an upfield shift. [b] Derived from the data reported by J. Meinwald, S.S.Labana, L.L.Labana and G.H.Wahl, Jr., Tetrahedron Letters. No. 23, 1789 (1965). [c] K.Kitahonoki, K.Kotera, Y.Matsukawa, S.Miyazaki, T.Okada, H. Takahashi and Y.Takano, Tetrahedron Letters No. 16, 1059 (1965). [d] S.J.Cristol and R.K.Bly, J. Amer. Chem. Soc. 82, 6155 (1960).

bridgehead protons. The divergence can result from the difference in the molecular geometries of XI, XII, and XIII, because the shielding of the bridgehead protons by an introduced three-membered ring might be highly sensitive to a slight change in the geometry of the tricyclic ring.*[5] By comparing the long-range anisotropic shielding effects of an aziridine ring with those of an epoxide ring (see TABLE II), it should be especially noted that the diamagnetic shielding parameter (ΔX value) in the direction perpendicular to the plain of the three-membered ring is larger in the case of an aziridine ring than in that of an epoxide ring. This difference evidently results from the nature of heteroatoms in the rings. In connection with this point, the anisotropic shielding effects of other kinds of three-membered rings are under active research in this laboratory.

REFERENCES

1. For examples, see P.M.Subramarian, M.T.Emerson and N.A.LeBel, J. Org. Chem. **30**, 2624 (1965); J.C.Davis, Jr. and T.V.Van Auken, J. Amer. Chem. Soc. **87**, 3900 (1965).
2. K.Tori, Y.Hata, R.Muneyuki, Y.Takano, T.Tsuji and H.Tanida, Canad. J. Chem. **42**, 928 (1964).
3. K.Tori, K.Aono, Y.Hata, R.Muneyuki, T.Tsuji and H.Tanida, Tetrahedron Letters No. 1, 9 (1966).
4. K.Tori, K.Kitahonoki, Y.Takano, H.Tanida and T.Tsuji, Tetrahedron Letters No. 11, 559 (1964).
5. K.Tori, K.Kitahonoki, Y.Takano, H.Tanida and T.Tsuji, Tetrahedron Letters No. 14, 869 (1965).
6. K.Tori and K.Kitahonoki, J. Amer. Chem. Soc. **87**, 386 (1965).
7. T.Goto, A.Tatematsu, Y.Hata, R.Muneyuki, H.Tanida and K.Tori, Tetrahedron **22**, (1966), in press.
8. G.V.D.Tiers, Characteristic nuclear magnetic resonance " shielding values" for hydrogen in organic structures Minesota Mining and Manufacturing Co., St. Paul, Minn. (1958).

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*[5] For discussions on this point, refer to Refs. (5, 6).