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NMR STUDIES OF BRIDGED RING SYSTEMS. IV.*[1] EPOXIDES*[2]

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IN recent years the ring current of a three-membered ring in a strong magnetic field has been the subject of a controversy (1,2). Roberts and coworkers (3) have reported on the basis of theoretical calculations of ring-current effects on chemical shifts in cyclopropanes that the comparison between experiment and theory cannot be taken as establishing the existence of ring current in cyclopropanes, but the trends are reasonably consistent with a ring-current effect. An epoxide ring has also been reported to have a ring current (4,5). From the present NMR study of some epoxides of bridged ring systems, we have found that there are some factors other than the ring current in the shielding effects of an epoxide ring upon neighboring protons.

Fig. 1 shows the NMR spectra*[3] of benzobicyclo(2.2.2)octene (I) (6,7) and its two isomeric epoxides (II and III) (6). The configurations of these epoxide rings were established by their spectra. Signals of the epoxidic protons H_2 and H_3 superimposed on the bridge-head proton signal appear as almost one peak at 6.59 τ in II and 6.67τ

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[1] Part III, K. Tori, Y. Takano and K. Kitahonoki, to be published.

[2] In this paper, the numbering and configurations of the compounds concerned are represented as shown in Figs. 1 and 2 for convenience (endo, exo, syn and anti are abbreviated as n, x, s and a, respectively).

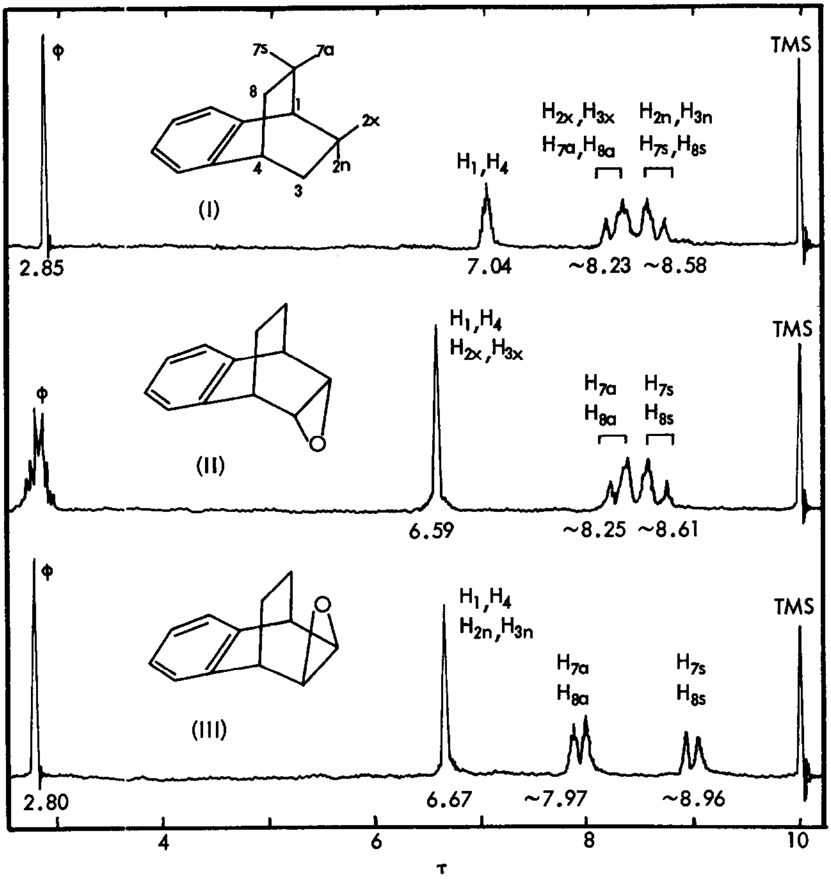

Fig. 1.*[3] NMR spectra of benzobicyclo(2.2.2)octene (I)*[4] and its epoxy derivatives (II and III) at 60 Mc in $CDCl_3$ (10%)

[*3] NMR spectra were taken with a Varian A-60 spectrometer, the calibration of which was checked according to the Tiers and Hotchkiss method (8). Chemical shifts are expressed in τ-values. Accuracies are within ±0.02τ.

[*4] NMR data and signal assignment procedures of the compounds I, IV and VI have been presented in Ref. (7).

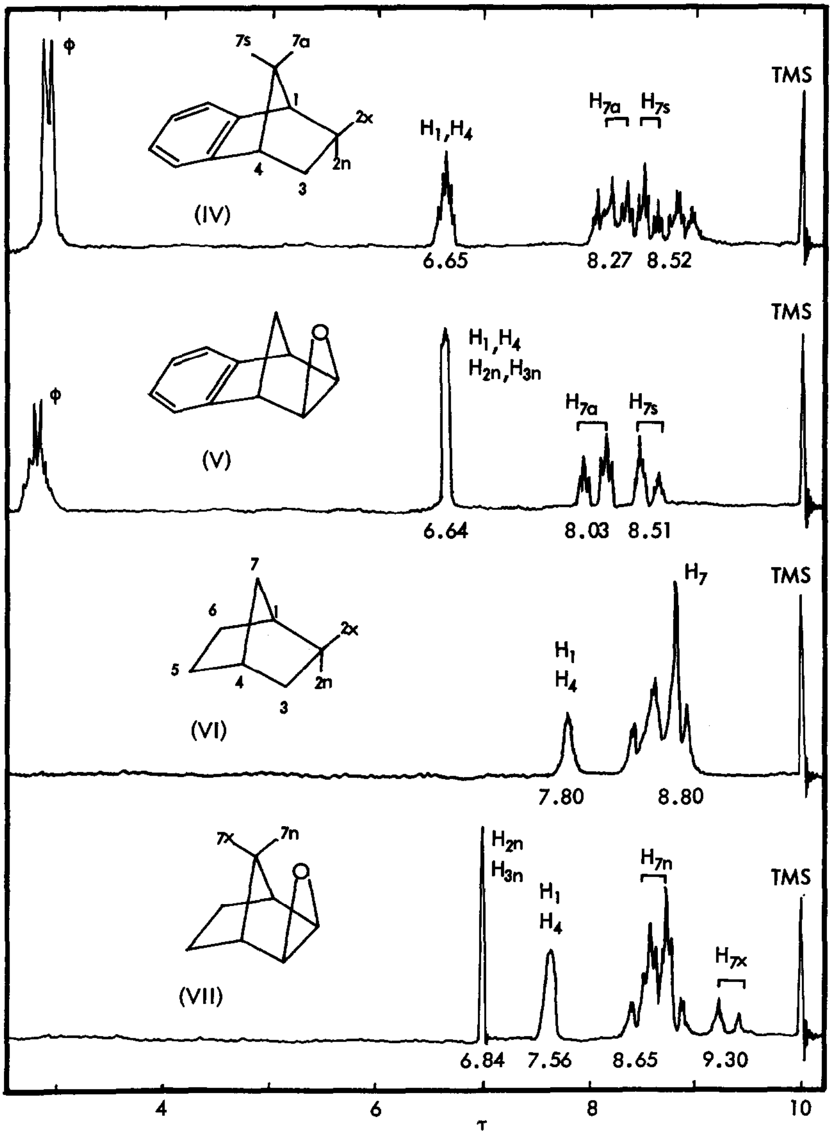

Fig. 2. *[3] NMR spectra of benzobicyclo(2.2.1)heptene (IV),*[4] bicyclo(2.2.1)heptane (VI)*[4] and their epoxy derivatives (V and VII) at 60 Mc in $CDCl_3$ (10%)

in III. *The ring current of the fused benzene ring in benzobicyclo(2.2.2)octenes is* known to shield *endo* (or *syn*) protons and to deshield the corresponding *exo* (or *anti*) protons (7).*[1] Calculations of the effects upon epoxidic protons using the Johnson-Bovey method (9) and Dreiding models were successfully carried out, showing the applicability of the above principle to the present cases. Since in this case shielding effects of the benzene ring upon the protons H_7 and H_8 in II should be equal to those in III, differences in the chemical shifts*[5] of these protons between II and III are entirely due to the effects of their epoxide rings. The *exo* epoxide ring exerts *significant effects on the protons* H_7 *and* H_8*, whereas the shielding effect of the corresponding* *endo* epoxide ring is slight. Thus the signals of protons H_{7a} and H_{8a} in III are shifted downfield by about 0.26 p.p.m. and those of protons H_{7s} and H_{8s} upfield by about 0.38 p.p.m. by the epoxide ring.

Fig. 2 shows the spectra of benzobicyclo(2.2.1)heptene (IV) (7) and its *exo* epoxide (V) (10). The epoxidic and bridge-head proton signals in V appear as almost one peak at 6.64τ. The AB type signals at 8.03τ and 8.51τ were assigned to the bridge protons H_{7a} and H_{7s}, respectively, because the two triplet peaks ($|J_{7a,7s}|=8.8$ c.p.s.; $J_{1(4),7a}=1.5$ c.p.s.) *of the former indicate lack of long-range spin couplings* whereas the two multiplet peaks of the latter show the existence of the couplings with the protons H_2 and H_3.*[6] Thus the signal of the proton H_{7a} is shifted downfield by 0.24 p.p.m. due to the introduction of the *exo* epoxide ring, whereas no significant effect is observed on the signal of the proton H_{7s}. Similarly, by comparison of the spectrum of bicyclo(2.2.1)heptane (VI) (7) with that of its *exo* epoxide (VII) (12) (see

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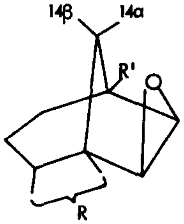
*[5] Approximate chemical shifts of these protons on the bridges are estimated in a manner similar to that previously reported (7).

*[6] Recently, the presence of the long-range spin coupling between protons H_{7s} and H_{2x} (H_{3x}) was observed (7,11).

Fig. 2), the signals of the protons H_{7n} and H_{7x} in VII are estimated to be shifted downfield by 0.15 p.p.m. and upfield by 0.50 p.p.m., respectively, from the signal position of the protons H_7 in VI.

Our data clearly show that an epoxide ring does shield the protons H_{7s} (H_{8s}) in III and H_{7x} in VII which are situated right above the plain of the epoxide ring. This is ascribed to a ring-current effect of the epoxide ring. The bridge protons H_7 and H_8 in II and H_5 and H_6 in VII are located at positions where the ring current can not exert marked effects. The fact that no difference was observed in the chemical shifts of the protons H_{7s} between IV and V is probably due to compensation of the change in the deshielding effect of the benzene ring caused by the alteration of molecular geometry, and the shielding effect of the epoxide ring. However, such a change would not significantly contribute to the signal shifts in the other compounds. On the other hand, the protons H_{7a} (H_{8a}) in III and V and H_{7n} in VII, which are situated at a very close position to the oxygen atom of the epoxide ring, are fairly deshielded by the epoxide ring. This observation cannot be explained by the ring current that is expected to give a more shielding effect. A plausible explanation is that a 1,3-diaxial interaction (13) between the relevant proton and the oxygen atom deshields the proton predominantly. Further the lone-pair electrons of the oxygen atom of an epoxide ring probably play a role in the above deshielding.*[7]

Our results described here are quite contrary to the recent report by Jefferies, et al. (5) who have assigned a doublet signal at a higher field (about 9.4τ) to the proton $H_{14\alpha}$ in some epoxides of diterpene beyrol



(VIII)

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*[7] It has been reported that excitation of lone-pair electrons of the nitrogen atom in the pyridine molecule induces the paramagnetic moment which mainly causes a downfield shift of the α-proton signal of pyridine (14).

derivatives (VIII) which have a bicyclo(3.2.1)octane skeleton. We suggest this doublet is due to the proton $H_{14\beta}$.

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