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The NMR spectra of some epoxides

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The NMR spectra of some epoxides

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The high resolution NMR spectra of a series of eight epoxides has been studied. Five of these, with the epoxide group axially affixed to a saturated ring, show ABX spectra and the analysis provides accurate values for the NMR parameters of the three-spin system. These are then compared with the data in the literature. Three of the epoxides, with the epoxide group equatorial to the ring, show, however, AA'B or AA'K spectra and cannot be interpreted explicitly without extensive fitting with machine calculations.

Recently there has been considerable interest [1, 2, 3] in obtaining experimental values for proton–proton coupling constants to serve as aids in the development of a proper theoretical treatment [2, 4, 5] of electron-coupled I . I interactions. With this in mind, Reilly and Swalen [6] have examined in detail four epoxides and Gutowsky *et al.* [2] have studied one of these, styrene oxide†. We have studied a series of eight epoxides of the form:

$$[B]H \qquad\qquad R$$
$$\diagdown\!{}_\beta \qquad {}_\alpha\!\diagup$$
$$C \;-\; C$$
$$\diagup \diagdown \diagup \diagdown$$
$$[A]H \qquad O \qquad H[X]$$
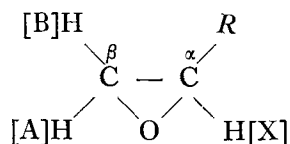
where R is a saturated cyclic alcohol containing no protons on the carbon bonded to the epoxy group. The eight compounds were the four isomeric (2-methyl-1-hydroxy-cyclohexyl)-ethylene oxides (I–IV) and four of the eight possible 1-hydroxy-decalyl-ethylene oxides (V–VIII) [7–11]‡.

The high resolution 60 Mc/s NMR spectra were taken in degassed CCl_4, with the exception of VI which was taken in degassed $CDCl_3$, and referred to internal hexamethyldisiloxane. Frequency shifts were measured by audio sideband interpolation sweeping upfield and downfield on alternate calibrations. Four calibrations were made for each spectrum. The small quantities of the compounds available caused some difficulties but the standard deviations of the peak separations within a single multiplet were less than 0·15 c/s and between peaks in separate multiplets (affecting the screening parameters only) less than 0·30 c/s. Spectra were also taken at 40 Mc/s, providing properly corresponding data.

† These authors have also examined propylene oxide but with an incomplete analysis due to the complexity of the spectrum and for this reason it will not be included in our discussion here. However, they do show the A proton to be to low field from the B proton for an hydrocarbon R group contrary to our data presented below.

‡ The structural formulae and several spectra of the compounds are given in ref. [11] according to the same system of numbering (I–VIII) as we employ here.

Since the epoxide structure is linked to a tertiary ring carbon and since we can neglect long-range couplings, the epoxy group protons can be considered as a closed system of three interacting spins. By analogy with data from vinyl compounds [12] we expect a spectrum of the form ABX [13] with the protons assigned as above; the X proton should lie to lowest field and the A proton to highest field. The first expectation has been verified by the four epoxides of ref. [6] but the second has only held for glycidonitrile and has been contradicted by the other three epoxides. We shall make our assignments based upon the experimental observation [6] that $J_{cis} = J_{AX} > J_{trans} = J_{BX}$ and upon the assumption that the X proton (observed to be to low field) is the one on the α carbon atom from the analogy with vinyl compounds.

In five of these epoxides† the spectrum is of the expected ABX type with either 11 or 12 non-overlapping peaks in each spectrum spread over a minimum of 32 c/s. From the data and ABX calculations‡ the NMR parameters as listed in the table are obtained. The coupling constants are probably valid to ± 0.25 c/s and the chemical shifts to ± 0.5 c/s.

From these data and the two assumptions above we observe that proton B does lie to low field from proton A in agreement with the vinyl compounds and contrary to three of the four epoxides previously studied. Thus an alkyl substituent can have the same effect on the chemical shift for epoxy protons as it has for vinyl protons. We further note that the screening parameter for the X proton is changed the most by the different substituents and that the sum of the screening parameters for the A and X protons is not relatively constant over the series, both contrary to the conclusions of Reilly and Swalen.

In three of these epoxides instead of the 12-peak ABX spectrum we find a six- or seven-peak AA'B or AA'K spectrum with all the peaks contained within 19 c/s. The six-peak spectra of (trans-2-methyl-1-hydroxy-cyclohexyl)-ethylene oxide, m.p. 75–75·5° (III), and (1α-hydroxy-9β-H)-trans-decalyl-ethylene oxide, m.p. 116·5–117·5° (VI) are almost of A_2B form (with B to low field) centred on 156·2 and 162·6 c/s respectively. (The latter is taken in $CDCl_3$ which should be corrected to ~ 155 c/s for comparison with data taken in CCl_4 [14].)

(Trans-2-methyl-1-hydroxy-cyclohexyl)-ethylene oxide, m.p. 40·5–41° (IV), has an AA'K spectrum containing seven peaks† with the peak for the K proton lying to low field. An explicit analysis of this spectrum is not feasible without

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† The sample of II given us was found to contain a mixture of 55 per cent (probably of) I and 45 per cent II. (This mixture was originally considered to be a mixture of II [11].) We were unable to separate these but could, with difficulty, distinguish parts of the two sets of multiplets. Only the approximate values as indicated in the table could be determined. In this compound (or rather mixture of compounds) the hydroxyl peak is rather independent of concentration and only slightly dependent on temperature. It is rather broad and over-laps the epoxy proton peaks—it is (at room temperature) 0·4 p.p.m. to lower field than any of the other hydroxyl proton peaks. Probably there is rather strong intra-molecular bonding involved, perhaps between the hydroxyl proton and the epoxy oxygen.

‡ It will be observed from the work of Reilly and Swalen that the error introduced into J_{AX} and J_{BX} by using an ABX calculation instead of the exact ABC calculation is small unless $\sigma_A - \sigma_B$ or $\sigma_B - \sigma_X$ is very small. VII and VIII have these values in the range of those for styrene oxide in which the agreement between the two calculations is within 0·1 c/s, and I and V should admit an error of < 0.2 c/s. The error in J_{AX} and J_{BX} in IV (below) should be larger and certainly accounts for the apparent equality of these two coupling constants. In all cases the error introduced into J_{AB} and the screening parameters should be < 0.05 c/s.

Compound	J_{AB}	J_{AX}	J_{BX}	$\eta H_0(1-\sigma_A)$	$\eta H_0(1-\sigma_B)$	$\eta H_0(1-\sigma_X)$
I (cis-2-methyl-1-hydroxy-cyclohexyl)-ethylene oxide, m.p. 42·5–43°	5·69	3·51	2·81	153·0	165·0	177·3
II (cis-2-methyl-1-hydroxy-cyclohexyl)-ethylene oxide, b.p. 88–9°/10 mm	~5·7	$\|J_{AX}\dagger + J_{BX}\|\dagger \approx 6.4$		$\sim 15 - \frac{\delta}{2}\dagger$	$\sim 151 + \frac{\delta}{2}\dagger$	~180
V (1α-hydroxy-9α-H)-1-1 trans-decalyl-ethylene oxide, m.p. 112–112·5°	5·58	3·61	2·79	155·3	166·7	181·9
VII (1α-hydroxy-9 β-H)-cis-decalyl-ethylene oxide, m.p. 100–101°	5·55	3·72	2·78	152·8	161·7	194·0
VIII (1α-hydroxy-9 β-H)-cis-decalyl-ethylene oxide, m.p. 88–90°	5·50	3·75	2·89	156·7	166·9	193·3
IV (trans-2-methyl-1-hydroxy-cyclohexyl)-ethylene oxide, m.p. 40·5–4·1°	$\dfrac{\delta^2 - 0.7}{1.7}$	~3·45	~3·45	$147\cdot1 - \frac{\delta}{2}\dagger$	$147\cdot1 + \frac{\delta}{2}\dagger$	160·9
Range of parameters (excluding II and IV)	0·19	0·24	0·10	3·9	5·2	16·0

Epoxide NMR parameters.   The data are given in c/s referred to internal hexamethyldisiloxane.

† These values could not be determined from the spectra.

machine calculations because of the inability to observe the several peaks of low intensity. However, it is possible, based on an ABX calculation to determine J_{AX}, J_{BX}, $\eta H_0(1-\sigma_X)$, $\frac{1}{2}\eta H_0(2-\sigma_A-\sigma_B)$ and a linear equation relating J_{AB} to $\delta = \eta H_0(\sigma_A-\sigma_B)$. These values are also given in the table except that the assignment of resonances to particular protons on the epoxide structure is chosen only to be consistent with the other assignments. It is interesting to note that $J_{AX}+J_{BX}$ (which is independent of the error in either of the coupling constants considered separately†) is 0·3 c/s greater than the same sum for any of the other molecules in the series. The range of $J_{AX}+J_{BX}$ for the six molecules is 6·3–6·9 c/s.

The original assignments of cis- and trans- configurations (for the non-hydroxyl substituents) of I–IV were verified by chemical conversion to the known cis- and trans-1,2-dimethylcyclohexanols. By conformational analysis I and II are expected to have their epoxy groups axial and III and IV are expected to have their epoxy groups equatorial. From our evidence, therefore, when the epoxy group is equatorial to the ring the α proton is > 0·25 p.p.m. to high field from its position when the epoxy group is axial‡ thus overlapping the peaks from the β protons and causing an ABX spectrum to collapse into an AA′B or AA′K spectrum. The pair of β protons also coalesce and contribute in a major way to the reduction in the number of peaks of the spectra. The explicit expression of this shift has not been determined, but it is the cause of the AB part of the ABX spectrum's going into the AA′ part of the AA′K spectrum. From the instances examined here this effect is very definite and specific and can serve as a method for identifying conformations of expoxy groups. On the basis of this, with Dr. Akhrem [11] we have reversed the configurational assignments of V–VIII which were previously identified only by qualitative chemical information. The corrected assignments have been used here.

Note added in proof.—It is unfortunate that we have used here the nomenclature AA′K, etc. as consistent with ref. [6] for which A′ signifies a nucleus with chemical shift slightly different from that of A. In more recent work, the author and others have found it more meaningful to use a prime to indicate a nucleus which has the same chemical shift as the unprimed nucleus but which is not magnetically equivalent to it: e.g. 1, 1-difluoroethylene and butadiene-1, 3 are

† The peaks relative to internal hexamethyldisiloxane were at: 145·05, 145·9, 148·5, 149·35, 157·5, 160·87, 164·87 c/s with appropriate intensities, and are assigned to transitions 3(A), 5(B), 4(A), 6(B), 9(X), 10–11(X), 12(X) respectively according to ref. [13]. The equation relating J_{AB} and δ is: $1·7J_{AB}+0·7=\delta^2$ with $\delta > 0$. For example: $J_{AB}=5·7$ c/s means that $\delta = 3·2$ c/s.

‡ This is analogous to the observation [14] that in 1, cis-3, trans-5-trimethylcyclohexane the protons on the axial methyl group are 0·14 p.p.m. deshielded from the protons on the equatorial methyl groups. With the epoxides, of course, the α-proton does not have the same time-average positions as the proton in the methyl groups.

called AA'XX' and AA'BB'XX' systems respectively and not A_2B_2 and $A_2B_2X_2$. This is to alleviate confusion between 'chemical equivalence' and 'magnetic equivalence'.

REFERENCES

[1] KARPLUS, M., ANDERSON, D. H., FARRAR, T. C., and GUTOWSKY, H. S., 1957, *J. chem. Phys.*, **27**, 597.
[2] GUTOWSKY, H. S., KARPLUS, M., and GRANT, D. M., 1959, *J. chem. Phys.*, **31**, 1278.
[3] MUSHER, J. I., 1961, *J. chem. Phys.*, **34**, 594.
[4] KARPLUS, M., and ANDERSON, D. H., 1959, *J. chem. Phys.*, **30**, 6.
[5] KARPLUS, M., 1959, *J. chem. Phys.*, **30**, 11.
[6] REILLY, C. A., and SWALEN, J. D., 1960, *J. chem. Phys.*, **32**, 1378.
[7] AKHREM, A. A., 1959, *Bull. Acad. Sci. U.R.S.S.*, 750.
[8] NAZAROV, I. N., and AKHREM, A. A., 1958, *J. gen. Chem.*, Moscow, **28**, 1791.
[9] NAZAROV, I. N., KAMERNITZKII, A. V., and AKHREM, A. A., 1958, *J. gen. Chem.*, Moscow, **28**, 1458.
[10] NAZAROV, I. N., ALEKZANDROVA, G. V., and AKHREM, A. A., 1948, *J. gen. Chem.*, Moscow, **28**, 2187, 2199.
[11] MUSHER, J. I., and AKHREM, A. A., 1960, *C.R. Acad. Sci. U.R.S.S.*, **134**, 354.
[12] ALEXANDER, S., 1958, *J. chem. Phys.*, **28**, 358.
[13] POPLE, J. A., SCHNEIDER, W. G., and BERNSTEIN, H. J., 1959, *High-Resolution Nuclear Magnetic Resonance* (New York: McGraw-Hill Book Company Inc.).
[14] MUSHER, J. I., unpublished results.