Carbon-13 Nuclear Magnetic Resonance Studies on Polyepoxides Derived from Singlet Oxygen Addition to Indenes

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Abstract: The carbon-13 nmr spectra of a number of common epoxides were studied at 63.1 MHz. These were used as models for the assignments of the spectra of the di-, tri-, and tetraepoxides resulting from the reaction of singlet oxygen with substituted indenes.

Carbon-13 nuclear magnetic resonance (cmr) spectroscopy is rapidly becoming an important method for determining the structures of organic molecules.[1-3] Recent work concerning the addition of singlet oxygen to substituted indenes[4,5] has provided a synthetic route to a series of compounds containing two, three, and four epoxide linkages whose structures lend themselves to study by cmr spectroscopy.

Although the carbon chemical shifts of only a few epoxides have been reported,[6] the chemical shifts of many oxygen-containing compounds are known and the chemical shifts of some selected compounds are listed in Table I. A comparison of the chemical shifts

Table I. Carbon-13 Chemical Shifts for Oxygen-Containing Heterocycles and Related Compounds

Compd	^{13}C chemical shifts (ppm downfield from TMS)		
	α	β	γ
Ethylene oxide[a]	39.7		
Trimethylene oxide[a]	72.8	23.1	
Tetrahydrofuran[a]	68.6	26.7	
Tetrahydropyran[a]	69.7	27.9	25.1
1,4-Dioxane[b]	67.4		
Diethyl ether[c]	67.4	17.1	
1,2-Dimethoxyethane	72.0 (CH$_2$) 59.0 (CH$_3$)		
Ethylene glycol[d]	63.4		

[a] Reference 1, p 270. [b] Reference 1, p 49. [c] Reference 1, p 144. [d] Reference 1, p 143.

of the epoxide carbons in these compounds shows that the ethylene oxide carbons are more shielded by about 30 ppm than the α carbons of acyclic and larger-ring oxides. Since this effect is similar to that observed for cyclopropane with respect to larger carbocyclic rings, it has been suggested that this large shielding term is due to the combined effects of a change in bond hybridization, ring strain, and the existence of a ring current in the three-membered ring.[7] This latter effect probably

contributes least to the observed chemical shift difference.

Experimental Section

The carbon-13 Fourier transform nmr spectra described in this paper were obtained at 63.1 MHz using a superconducting magnet with a field of 59 kG.[8] The hydrogens were usually noise-decoupled with a power of 15 W at 251 MHz. Single frequency and off-resonance decoupling experiments were conducted with a proton-decoupling power of 1-10 W. The carbon chemical shifts are all given in ppm downfield from an internal tetramethylsilane (TMS) standard. All samples were examined at concentrations of 1-3 M in CDCl$_3$ solution at room temperature. The preparation of these compounds is described elsewhere.[5]

Results and Discussion

Common Epoxides. The carbon chemical shifts of several common epoxides whose spectra were used as additional models for the present study are found in Figure 1. From these data, we note that increasing substitution tends to deshield the epoxide carbon. The change in the substituent from hydrogen to methyl (ethylene oxide to propylene oxide) causes a downfield shift of the epoxide carbon by about 9 ppm. Substitution on one of the epoxide carbons affects both, but the tertiary carbons are normally more deshielded than are the secondary carbons. In the substituted propylene oxide systems, the substitution of electronegative groups on carbon 3 causes a downfield shift in the resonance corresponding to carbon 2 but causes little change in the chemical shift of carbon 1. These results are similar to those previously reported for chemical shift effects in haloalkanes.[9]

The substitution of aromatic groups at an epoxide carbon results in a noticeable change in the chemical shifts of both epoxide carbons. A comparison of the chemical shift of the carbons in ethylene oxide to the shifts in styrene oxide shows that replacing a hydrogen with a phenyl causes the epoxide carbons to be deshielded by about 11 ppm. This effect seems to be additive since the replacement of second epoxide hydrogen by a phenyl on going from styrene oxide to *trans*-stilbene oxide results in the deshielding of both epoxide carbons by another 11 ppm.

The carbon chemical shifts of cyclohexene oxide are also listed in Figure 1. Electron diffraction studies have determined that this compound exists in the half-chair conformation.[10]

(1) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists," Wiley-Interscience, New York, N. Y., 1972.

(2) J. B. Stothers, "Carbon-13 NMR Spectroscopy," Academic Press, New York, N. Y., 1972.

(3) L. F. Johnson and W. C. Jankowski, "Carbon-13 NMR Spectra," Wiley-Interscience, New York, N. Y., 1972.

(4) C. S. Foote, S. Mazur, P. A. Burns, and D. Lerdal, *J. Amer. Chem. Soc.*, **95**, 586 (1973).

(5) P. A. Burns, H. S. Brown, N. R. Easton, Jr., C. S. Foote, and S. Mazur, to be submitted for publication.

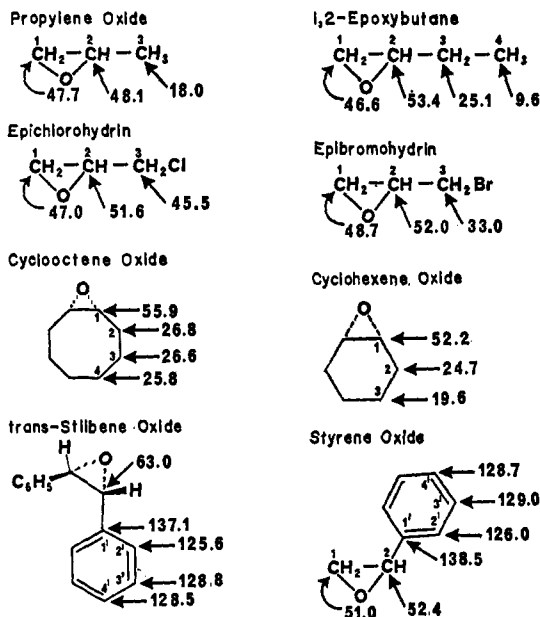(6) Reference 1, p 35; ref 2, p 270; ref 3, p 29.

(7) Reference 2, p 270.

(8) F. A. L. Anet, C. H. Bradley, and G. W. Buchanan, abstract of paper presented at the 11th Experimental NMR Conference, Pittsburgh, Pa., April 1970.

(9) Reference 2, p 133.

(10) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Wiley, New York, N. Y., 1965, p 111.

Propylene Oxide

I,2-Epoxybutane

Epichlorohydrin

Epibromohydrin

Cyclooctene Oxide

Cyclohexene, Oxide

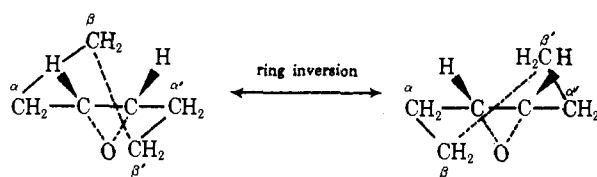trans-Stilbene Oxide

Styrene Oxide

Figure 1. Carbon-13 chemical shifts for some common epoxides. Chemical shift values are given in ppm downfield from internal TMS.

half-chair conformation of cyclohexene oxide

In this conformation, the lone pair electrons on the oxygen are spatially proximate to both of the β carbons since ring inversion is rapid at room temperature. This effect should cause a marked shielding of the β carbons and presumably is the reason for their pronounced upfield shift of 7 ppm relative to cyclohexane (chemical shift 26.9 ppm).[11]

Diepoxides. The product (1,6) of the reaction of two molecules of singlet oxygen with a substituent indene contains two epoxides and a single endoperoxide bridge.[12,12a] The carbon chemical shift data for these compounds are in Table II. Figure 2 gives a graphical presentation of the change in the chemical shifts of the carbons of the molecular skeleton relative to the change of substituents on the five-membered ring.

The methyl, methylene, methine, and quaternary carbons were assigned using off-resonance proton decoupling. Carbons of similar chemical shifts, such as the three epoxide methine carbons in compound 1, were assigned using selective proton decoupling with a power of 1 W. In these experiments, a proton whose resonance had been assigned in the proton spectrum was determined to be coupled to a particular carbon, thus

(11) Reference 1, p 45.

(12) These compounds exist as a pair of dl optical isomers. Since the carbon chemical shifts are independent of optical activity, only one enantiomer of each compound is shown and discussed.

(12a) NOTE ADDED IN PROOF. On-going X-ray crystallographic studies on one of two isomeric tetraepoxides prepared from 1,2-dihydro-4-phenylnaphthalene show that the epoxide group analogous to the 2,3-epoxide in compounds 1–18 has the opposite stereochemisty to that shown for these compounds in this paper. The stereochemistry of the other three epoxide groups is the same. No definitive X-ray structures have been completed on the compounds discussed in this paper.
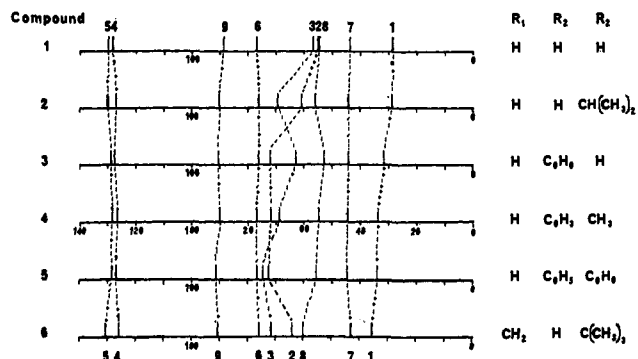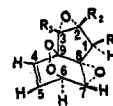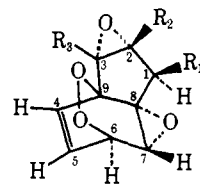
Figure 2. Carbon-13 chemical shifts of the diepoxides. Shown in ppm downfield from internal TMS. Chemical shift assignments are shown by the numbers above and below the spectra.

Table II. Carbon-13 Chemical Shifts of Diepoxides 1–6

Carbon[a]	Chemical shifts (ppm) of diepoxides					
	1	2	3	4	5	6
1	28.6	28.6	31.4	33.8	34.0	35.6
2	55.1	60.7	72.0	71.8	72.5	64.0
3	56.5	69.0	62.9	68.7	74.6	71.4
4	128.3	126.9	127.6	126.6	126.9	125.9
5	129.7	129.7	128.7	128.3	128.3	130.6
6	76.7	76.0	76.1	76.7	76.7	75.8
7	43.6	43.9	44.1	44.3	44.6	43.0
8	54.7	55.8	52.5	54.7	55.4	60.0
9	88.6	90.0	90.3	90.0	91.3	90.6
R₁(CH₃)						14.4
R₃α		26.5		10.5		32.4
R₃β		18.8				27.5
1'			132.5	134.2		
2'			126.2	126.6		
3'			128.7	128.3		
4'			128.5	128.0		

[a] Primed numbers refer to carbons of phenyl groups (1' = attachment carbon, 2' = ortho carbon, 3' = meta carbon, 4' = para carbon).

Compd	R₁	R₂	R₃
1	H	H	H
2	H	H	CH(CH₃)₂
3	H	C₆H₅	H
4	H	C₆H₅	CH₃
5	H	C₆H₅	C₆H₅
6	CH₃	H	C(CH₃)₃

allowing the assignment of that carbon. Carbons 2, 3, 6, and 7 were assigned in this manner.

Similar selective proton-decoupling experiments were used to determine the assignments of the vinyl carbons in 1 and 5. For example, in 1 the carbon with δ 128.3 was found to be attached to the proton with δ 6.50 while

the carbon with δ 129.7 was attached to the proton with δ 6.27. From the proton nmr spectra, the upfield proton in **1** was found to be coupled to H-6 with $J = 6.1$ Hz while the downfield proton was coupled to H-6 with $J = 1.4$ Hz. Since a coupling constant of 6.1 Hz is too large to be due to allylic coupling, it must be due to a vicinal coupling, and the upfield proton must be H-5. Thus, in **1**, C-5 has a chemical shift of 129.7 ppm while C-4 has a chemical shift of 128.3 ppm. The chemical shifts of the carbons in compounds **2**, **3**, **4**, and **6** were assigned by analogy with those in compounds **1** and **5**.

Compound **5** has phenyl substituents on carbons 2 and 3, with resonances at 72.5 and 74.6 ppm. The resonance at 72.5 ppm was assigned to C-2 since this gives C-2 a chemical shift similar to that of C-2 in compound **3**. If we note that the α and β effects should be the same for carbons 2 and 3 in **5**, then the C-2 resonance should also be upfield from that of C-3 in that compound by analogy with compound **1** in which this order has been proved by selective proton decoupling.

From the data presented in Figure 2, it is apparent that changing substituents on the five-membered ring causes little change in the chemical shifts of those carbons linked by the endoperoxide bridge (carbons 6 and 9) and the vinyl carbons (4 and 5). Carbon 7, which is spatially remote from the substituents, is also unaffected.

In this series, the average chemical shift for C-9 is 90 ppm while that for C-6 is 76.5 ppm. This difference would be expected since each carbon is linked to an oxygen atom of the peroxide bridge, and C-9 is quaternary whereas C-6 is tertiary.

Since these compounds are substituted on the five-membered ring, it is to be expected that carbons 2 and 3, to which the substituents are attached, would be the most affected; in fact, large α and β substituent chemical shift effects are observed for these two carbons. Carbon 1 exhibits a much larger α than β effect.

It is possible to describe the effects of the R_2 and R_3 substituents on carbons 2 and 3 through the use of a linear shift relation of the type developed by Grant and Paul.[13] In this equation, $\delta_c{}^i$ is the chemical shift of

$$\delta_c{}^i = B + \sum_j A_j n_{ij}$$

carbon i; A_j is the additive chemical shift parameter for the jth position, n_{ij} is the number of groups in the jth position relative to carbon i, and B is a constant set equal to the chemical shift of carbon i in the parent compound. Only four parameters are of concern—those for α- and β-phenyl groups and those for α- and β-methyl groups. The values for these parameters are found in Table III. While carbons 2 and 3 show both α and β effects, C-1 has a normal α effect but a much smaller β effect.

Table III. Additive Chemical Shift Parameters ("A" Parameters)

Substituent	A parameters (ppm)		
	Diepoxides	Tetraepoxides	Triepoxides
α-C_6H_5	+17	+12	+12
β-C_6H_5	+6	+3	+5
α-CH_3	+3	+7	+7
β-CH_3	+3	+4	+5

(13) D. M. Grant and E. G. Paul, *J. Amer. Chem. Soc.*, **86**, 2984 (1964); see also ref 2, p 55.

The epoxide carbons directly bonded to a phenyl group show an α effect but seem unaffected by β substituents. Carbon 8, another epoxide carbon, shows a large deshielding when there is a β substituent.

The compound containing two phenyl groups, **5**, is expected to show more erratic chemical shift behavior than the other compounds since the bulky phenyl groups cause the introduction of nonadditive steric contributions to chemical shifts.

Tetraepoxides. When the peroxides are heated, they rearrange to compounds containing four epoxide groups with the following structure.
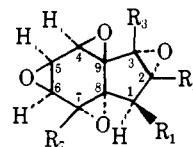
Compd	R_1	R_2	R_3	R_7
7	H	H	H	H
8	H	H	$CH(CH_3)_2$	H
9	H	C_6H_5	CH_3	H
10	H	C_6H_5	C_6H_5	H
11	CH_3	H	$C(CH_3)_3$	H
12	H	H	$CH(CH_3)_2$	CH_3

Table IV contains the carbon-13 chemical shifts for this class of compounds while Figure 3 gives a graphic presentation of the changes in the chemical shifts.

Table IV. Carbon-13 Chemical Shifts of the Tetraepoxide Compounds[a]

Carbon	Chemical shifts (ppm) of tetraepoxides					
	7	8	9	10	11	12
1	32.3	32.5	36.6	36.0	38.8	33.4
2	53.1	58.3	69.4	69.4	62.5	58.7
3	54.0	63.3	63.5	71.1	72.3	65.3
4	47.9	48.2	48.1	48.1	48.1	48.4
5	52.3	52.5	51.6	51.9	52.1	52.5
6	51.7	51.7	51.6	51.9	51.6	56.0
7	53.1	52.7	52.6	53.0	52.2	59.0
8	56.7	64.1	64.8	63.7	64.8	68.6
9	63.3	65.8	65.9	65.4	65.9	66.5
$R_1(CH_3)$					13.1	
$R_3\alpha$		22.6	8.4		32.0	22.8
$R_3\beta$		18.5/18.9[b]			27.6	18.6/18.7[b]
$R_7(CH_3)$						17.5
1'			134.6			
2'			126.6			
3'			128.7			
4'			128.3			

[a] Primed numbers as in Table III. [b] These assignments could be interchanged.

The assignments of the methine carbon chemical shifts of **7**, **8**, and **9** were made by selective proton decoupling techniques described earlier. The assignment of the C-7 resonance was confirmed by a comparison of the spectra of **8** and **12** which differ only in the presence of a 7-methyl group in **12**. The peaks at 48.4 and 52.5 ppm in **12** are essentially unchanged from **8** and correspond to the resonances from C-4 and C-5 which should not be affected by substitution at C-7. The resonance for C-6 should show a downfield shift due to the β effect and is found at 56.0 ppm. The resonance for C-7, now a quaternary carbon, is seen at 59.0 ppm. The chemical
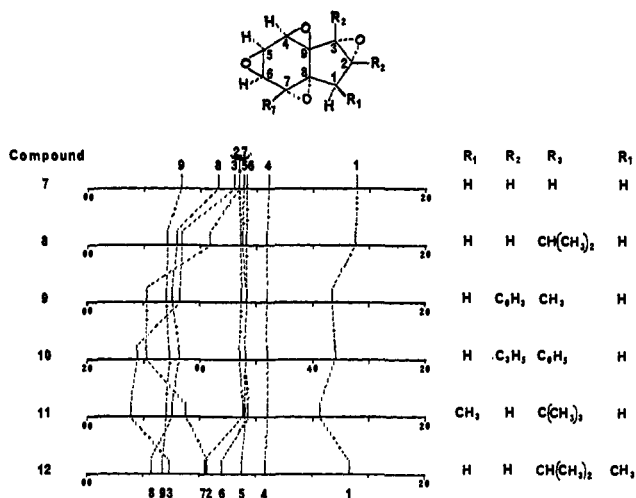
Figure 3. Carbon-13 chemical shifts of the tetraepoxides shown in ppm downfield from internal TMS. The numbers above the resonances for compound 7 and below those for 11 show to which carbon each line corresponds.

shift assignments in **10** and **11** were made by analogy with the other tetraepoxides.

The chemical shifts of carbons 2, 3, and 7 seem to follow an additive chemical shift equation with A parameters slightly smaller than those calculated for the diepoxides, as shown in Table III.

The agreement between calculated and experimental carbon chemical shifts in this series is quite good; however, the diphenyl compound, **10**, does not follow the linear chemical shift relation as well as the other compounds, as was found for the diepoxide series.

Triepoxides. When the peroxides are reacted with trimethyl phosphite, compounds containing three epoxide linkages are formed. These triepoxides have the following general structure.

Compd	R_1	R_2	R_3	R_7
13	H	H	H	H
14	H	H	$CH(CH_3)_2$	H
15	H	C_6H_5	CH_3	H
16	H	C_6H_5	C_6H_5	H
17	CH_3	H	$C(CH_3)_3$	H
18	H	H	$CH(CH_3)_2$	CH_3

The carbon-13 chemical shifts of the compounds of this class are found in Table V and a graphical presentation of these shifts is found in Figure 4.

The carbon chemical shifts in **13**, **14**, and **15** were assigned by techniques described previously. Particular attention was paid to C-7 and C-4. Preparation of **18** with a methyl substituent at C-7 enabled us to assign the carbon resonance at 49 ppm to C-7 unambiguously, thus leaving the epoxide methine resonance at 53 ppm for C-4. Single-frequency proton-decoupling experiments were undertaken to relate C-7 and C-4 to their respective protons and these experiments confirmed the
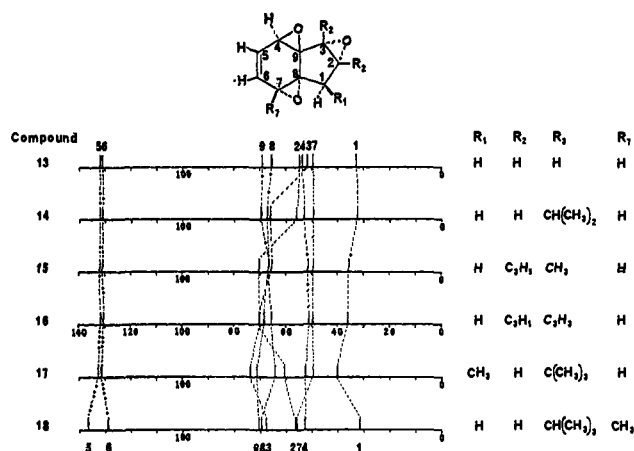
Figure 4. Carbon-13 chemical shifts of the triepoxides shown in ppm downfield from internal TMS.

Table V. Carbon-13 Chemical Shifts of the Triepoxide Compounds[a]

Carbon	Chemical shifts (ppm) of triepoxides					
	13	14	15	16	17	18
1	32.6	32.4	36.6	36.9	40.0	31.6
2	54.5	56.1	70.4	70.2	60.3	56.6
3	51.6	66.2	65.5	70.2	73.8	67.7
4	53.4	53.0	51.6	51.0	52.3	52.7
5	132.0	132.1	132.1	131.6	132.4	136.7
6	130.9	131.1	131.1	130.4	131.4	128.8
7	49.3	49.5	49.5	49.3	49.4	56.2
8	65.2	67.3	66.9	65.4	64.3	69.4
9	68.9	69.7	66.9	68.3	71.3	70.6
$R_1(CH_3)$					13.0	
$R_3\alpha$		21.6		7.0	32.1	22.3
$R_3\beta$		18.1/18.5[b]			27.6	18.5/18.7[b]
$R_7(CH_3)$						18.4[b]
1'				134.9		
2'				126.9		
3'				128.6		
4'				128.3		

[a] Primed numbers as in Table III. [b] These assignments could be interchanged.

original assignments. The assignments of the vinyl carbons were based on selective proton-decoupling experiments conducted after the proton assignment was confirmed by proton–proton decoupling experiments. The chemical shifts of **16** and **17** were assigned with the other triepoxides.

Carbons 2 and 3 show the expected behavior since their chemical shifts seem to follow a linear additive chemical shift equation. The A parameter values (see Table III) are very close to those calculated for the tetraepoxides compounds and are slightly smaller than those calculated for the diepoxides. The agreement between calculated and experimental chemical shifts is quite good (± 1 ppm) for all compounds except, once again, for the diphenyl compound. A comparison of the chemical shifts of the triepoxides and tetraepoxides shows that the chemical shifts of carbons 8 and 9 in compounds with a C-5–C-6 epoxide are upfield from those in compounds with a C-5–C-6 double bond.