Carbon-13 Nuclear Magnetic Resonance Spectra of Some Epoxides

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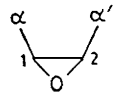
^{13}C N.m.r. data for 61 epoxides are tabulated, and substituent additivity values for prediction of epoxide carbon chemical shifts for simple epoxides are proposed.

No systematic study of ^{13}C n.m.r. spectra of epoxides has been published, although standard texts [1] give isolated examples and some recent papers have dealt with a small number of different types.[2] Since we had available a range of epoxides, their ^{13}C n.m.r. spectra were obtained, primarily to investigate the influence of structure and stereochemistry on chemical shift of the epoxide carbon(s).

Results are listed in the Table. Also included for reference are assignments for the non-epoxide carbons and where these are tentative this is indicated by an appropriate superscript letter (see Table).

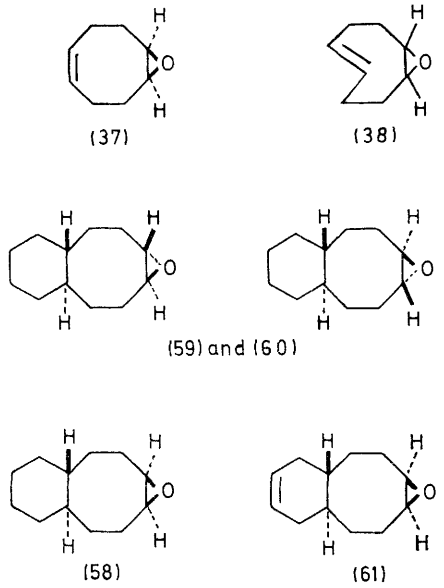
^{13}C N.m.r. chemical shifts for epoxide carbons are in the range 40—75 p.p.m. (downfield from tetramethylsilane). The carbons of ethylene oxide are most shielded, those of the substituted epoxides being relatively deshielded. The effects of alkyl and phenyl substitution can be discerned by examination of the results for compounds (1)—(23). Fair agreement (±2 p.p.m., better in many cases)



SCHEME Empirical substituent values (p.p.m.) for calculation of ^{13}C resonance of C-1 of a substituted epoxide. Basic value of ethylene oxide 40·8; for each 1-methyl group +7·0; for each 2-methyl group +7·0; for each additional α-alkyl group +4·0; for each additional α′-alkyl group −1·0; for each 1-phenyl +11·0; for each 2-phenyl +10·0; for geminal substitution −1·0; for *cis*-1,2-disubstitution −3·0; for *trans*-1,2-disubstitution 0·0.

with observed chemical shift for the epoxide carbon(s) of simple substituted epoxides can be obtained by employing the substituent values shown in the Scheme. Thus, as frequently found for ^{13}C n.m.r.,[1] the chemical shifts are influenced by substituents in a simple additive manner.

Epoxide carbon shifts for epoxycycloalkanes (24)—(28) show progressive deshielding along the series cyclohexane, cyclo-octane, cycloheptane, cyclopentane, and a similar trend is shown for the ring carbons of exocyclic epoxides (48)—(53). This trend does not correlate simply with ring strain (*cf.* strain energies of corresponding cycloalkenes [3]) and the effect is presumably of conformational origin.



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^{13}C Chemical shifts [a] of oxirans [b]

Compound †	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12	C-13
(1) Ethylene oxide	*40·8*												
(2) 1,2-Epoxypropane	*47·8*	*48·0*	18·1										
(3) 1,2-Epoxypentane	*46·8*	*52·0*	34·9	19·6	14·0								
(4) 1,2-Epoxyhexane	*46·8*	*52·2*	32·5	28·4	22·8	14·1							
(5) 1,2-Epoxyoctane	*46·8*	*52·2*	32·8	32·1	29·4	26·2	22·8	14·2					
(6) 1,2-Epoxydecane	*46·8*	*52·2*	32·8	32·1	29·8	29·8	29·5	26·3	22·9	14·2			
(7) 1,2-Epoxydodecane	*47·0*	*52·3*	32·7	32·1	29·8	29·8	29·8	29·8	29·6	26·2	22·9	14·2	
(8) *cis*-2,3-Epoxybutane	12·9	*52·4*											
(9) *trans*-2,3-Epoxybutane	17·6	*55·2*											
(10) 2-Methyl-1,2-epoxypropane	*54·5*	*53·9*	23·1										
(11) 2-Methyl-*cis*-2,3-epoxybutane	18·5	*58·1*	*59·9*	14·2	[24·8]								
(12) 2,3-Dimethyl-2,3-epoxybutane	21·2	*61·7*											
(13) 3-Chloro-1,2-epoxypropane	*46·8* [c]	*51·4*	45·4 [c]										
(14) 2-Ethyl-1,2-epoxybutane	*51·5*	*60·8*	26·8	8·8									
(15) *trans*-1,2-Di-t-butylethylene oxide		*63·1*	30·4	26·0									

TABLE (*Continued*)

	Compound †	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12	C-13
(16)	1-Phenyloxiran	*52·2*	*50·9*	[137·4	128·5 [c]	125·6 [c]	128·1]							
(17)	*cis*-1,2-Diphenyloxiran		*59·6*	137·1	127·7 [c]	126·8 [c]	127·5							
(18)	*trans*-1,2-Diphenyloxiran [g]		*62·7*	137·1	128·5 [c]	125·5 [c]	128·3							
(19)	1,1-Diphenyloxiran	*61·7*	*56·7*	[139·6	128·2 [c]	127·5 [c]	127·9]							
(20)	Tetraphenyloxiran		*73·8*	138·7	127·6 [c]	128·3 [c]	127·1							
(21)	2-Phenyl-1,2-epoxypropane	*56·7*	*56·7*	21·8	[141·5	128·4 [c]	125·4 [c]	127·4]						
(22)	2-Phenyl-1,2-epoxybutane	*55·2*	*60·7*	28·3	9·0	[140·3	128·3 [c]	126·1 [c]	127·4]					
(23)	2-Benzyl-3-phenyl-1,2-epoxypropane	*51·0*	*59·7*	40·3	136·9	129·8 [c]	128·3 [c]	126·6						
(24)	1,2-Epoxycyclopentane		*57·0*	27·3	18·4									
(25)	1,2-Epoxycyclohexane		*51·9*	24·7	19·7									
(26)	1,2-Epoxycycloheptane		*55·9*	29·2 [c]	24·6 [c]	31·2								
(27)	*cis*-1,2-Epoxycyclo-octane [g]		*55·6*	26·7 [c]	26·5 [c]	25·8 [c]								
(28)	*trans*-1,2-Epoxycyclo-octane		*59·5*	32·7 [c]	28·6 [c]	28·6 [c]								
(29)	1-Methyl-1,2-epoxycyclohexane	*57·1*	*59·2*	30·1 [c]	19·8 [d]	23·9 [d]	25·0 [c]	[20·2]						
(30)	1-Methyl-1,2-epoxycycloheptane	*60·6*	*62·8*	35·0 [c]	29·6 [d]	24·0 [d]	25·1 [d]	31·5 [c]	[24·5]					
(31)	1-Methyl-*cis*-1,2-epoxycyclo-octane [g]	*59·5*	*63·0*	31·5	26·7	25·4	26·2	26·2	28·0	[21·6]				
(32)	1-Methyl-*trans*-1,2-epoxycyclo-octane [g]	*59·0*	*64·1*	38·7 [c]	28·6 [c]	26·7 [c]	26·7 [c]	28·0 [c]	28·7 [c]	[18·6]				
(33)	1-Phenyl-*cis*-1,2-epoxycyclo-octane-	*62·8*	*61·9*	32·0	26·7 [c]	26·0 [c]	25·2 [c]	26·6 [c]	27·8 [c]	[141·2	128·2 [d]	127·2 [d]	127·5] [g]	
(34)	1,2-Epoxycyclopent-3-ene	*56·5*	*58·8*	137·6	131·5	35·6								
(35)	1,2-Epoxycyclohex-4-ene		*50·8*	25·2	121·7									
(36)	1,2-Epoxy-*cis*-cyclo-oct-3-ene	*53·5*	*57·9*	134·1	123·1	29·1 [c]	25·9 [c]	25·2 [c]	27·6 [c]					
(37)	1,2-Epoxy-*cis*-cyclo-oct-5-ene [h]		*56·5*	28·3 [c]	23·7 [c]	128·9								
(38)	1,2-Epoxy-*trans*-cyclo-oct-5-ene [h]	*54·9*	*54·5*	38·8 [c]	25·2 [c]	137·1 [d]	132·2 [d]	32·0 [c]	30·2 [c]					
(39)	*trans*-1,2-Epoxy-*cis*-cyclo-oct-5-ene [h]		*58·9*	29·1	25·5	130·7								
(40)	*cis*-1,2-*cis*-5,6-Diepoxycyclo-octane [h]		*56·0*	22·0										
(41)	*cis*-1,2-*trans*-5,6-Diepoxycyclo-octane [h]	*55·7*	*55·3*	27·5 [c]	27·2 [c]	*59·5*	*56·6*	26·7 [c]	25·2 [c]					
(42)	1,2-Dimethyl-1,2-epoxycyclohexane		*62·0*	31·4	20·9			[20·9]						
(43)	1,2-Dimethyl-1,2-epoxycyclohex-4-ene		*61·2*	32·2	129·6			[19·6]						
(44)	10-Oxatricyclo[4.3.1.0^{1,6}]-dec-3-ene	*65·4*	31·3	122·2				28·1	19·0					
(45)	11-Oxatricyclo[4.4.1.0^{1,6}]-undecane [i]	*62·1*	31·1	20·6										
(46)	*trans*-2-Hydroxy-9-oxabicyclo[6.1.0]nonane	*60·5*	71·3	35·1	26·9	26·5 [c]	25·5 [c]	23·8 [c]	*55·6*					
(47)	*cis*-2-Hydroxy-9-oxabicyclo[6.1.0]nonane	*57·4*	66·2	32·9	26·1 [c]	24·7 [c]	24·2 [c]	19·3 [c]	*57·0*					
(48)	1-Oxaspiro[2.4]heptane		*52·1*	*65·1*	32·6	25·4								
(49)	1-Oxaspiro[2.5]octane		*54·3*	*58·8*	33·8	25·0	25·5							
(50)	1-Oxaspiro[2.6]nonane		*55·5*	*60·3*	36·0	29·0	24·8							
(51)	1-Oxaspiro[2.7]decane		*55·6*	*59·2*	34·6	26·6	25·5	24·3						
(52)	*cis*-6-t-Butyl-1-oxaspiro-[2.5]octane		*53·4*	*57·8*	33·5	25·0	47·3	[32·5	27·6]					
(53)	*trans*-6-t-Butyl-1-oxaspiro[2.5]octane		*54·9*	*59·5*	34·1	26·7	47·4	[32·4	27·8]					
(54)	*exo*-2,3-Epoxynorbornane	36·8	*51·0*			25·3		26·3						
(55)	*endo*-2,3-Epoxynorbornane	37·7	*62·0*			25·5		50·4						
(56)	*exo*-2,3-Epoxynorborn-5-ene	43·4	*59·0*			141·0		40·4						
(57)	*endo*-2,3-Epoxynorborn-5-ene	43·0	*51·8*			130·7		61·8						
(58)	*trans,cis*-5-Oxatricyclo-[7.4.0.0^{4,6}]tridecane [h]	41·3 [c]	33·0 [d]	34·2 [d]	*57·0* [e]		*56·4* [e]	33·2 [d]	29·9 [d]	37·0 [c]	26·6 [f]	25·0 [f]	25·0 [f]	25·0 [f]
(59)	*trans,trans*-5-Oxatricyclo-[7.4.0.0.^{4,6}]tridecane (isomer 1) [h]	42·5	31·6 [c]	35·6	*59·3*						20·6	30·0 [c]		
(60)	*trans,trans*-5-Oxatricyclo-[7.4.0.0.^{4,6}]tridecane (isomer 2) [h]	42·5	37·3 [c]	37·5 [c]	*57·8*						26·2 [d]	27·3 [d]		
(61)	*trans,cis*-5-Oxatricyclo-[7.4.0.0^{4,6}]tridec-11-ene [h]	39·3 [c]	27·8 [d]	32·8 [d]	*56·4*		*55·4*	32·4	24·7 [d]	37·3 [c]	32·1	128·8	128·4	32·1

† Compounds (34)—(39) and (43) are named non-systematically to aid comparison of numerical data in the Table.

[a] In p.p.m. downfield from tetramethylsilane for solutions in $CDCl_3$ (50%). [b] Assignments in italics are for epoxide carbons; those in square brackets are for side chain carbons, numbering proceeding outwards from the branch point. [c–f] Ambiguous assignment, may be interchanged. [g] Sample provided by A. J. Bridges. [h] Sample provided by P. Newton. [i] Sample provided by S. R. Postle.

The effect of the epoxide ring on the ^{13}C chemical shift of remote carbon can sometimes be quite marked, *e.g.* in the epoxynorbornanes (54)—(57) where the most striking feature is the significant deshielding (> 20 p.p.m.) of the resonance attributable to C-7 in the *endo*-epoxides.

Overall molecular symmetry can provide a simple means of discriminating between stereoisomers on the basis of their ^{13}C n.m.r. spectra. Thus the epoxide (37) with a plane of symmetry only shows four lines compared with the eight-line spectrum of epoxide (38). Similarly the epoxides (59) and (60) with C_2 axes show six-line spectra and may be contrasted with the much more complex spectra shown by epoxides (58) and (61).

Note added in proof: Some of our data on the simpler epoxides are duplicated in a recent paper (D. R. Paulson, F. Y. N. Tang, G. F. Moran, A. S. Murray, B. P. Pelka, and E. M. Vasquez, *J. Org. Chem.*, 1975, **40**, 184). The downfield ^{13}C shift of C-7 in *endo*-norbornane epoxides (55) and (57) is even more striking in the light of γ-upfield shifts described recently (E. L. Eliel, W F. Bailey, L. D. Kopp, R. L. Willer, D. M. Grant, R. Bertrand, K. A. Christensen, D. K. Dalling, M. W. Duck, E. Wenkert, F. M. Schell, and D. W. Cochran, *J. Amer. Chem. Soc.*, 1975, **97**, 322).

EXPERIMENTAL

The carbon-13 n.m.r. spectra were obtained with a Bruker WH90 instrument operating at 22·63 MHz using broad band proton decoupling; in some cases off-resonance decoupling was employed to aid peak assignments. Chemical shifts were measured relative to internal tetramethylsilane for 50% solutions of the epoxide in $CDCl_3$.

Two general preparative methods were used to obtain epoxides which were not otherwise available: (a) epoxidation of the corresponding olefin with buffered peracetic acid,[4] (b) treatment of the corresponding ketone with dimethylsulphoxonium methylide.[5]

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