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CARBON-13 NMR SPECTRA OF SIMPLE GLYCIDIC ESTERS

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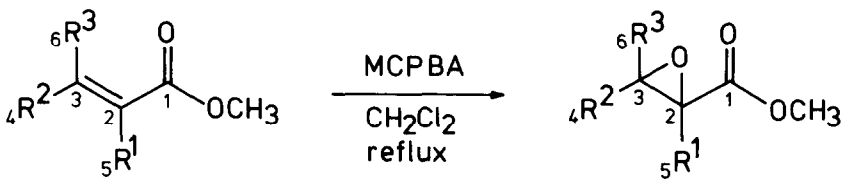
Summary: The line separations from geminal and vicinal CH-couplings in simple glycidic esters are found to be within narrow ranges. They can be used for the assignment of carbon resonances and epoxide configurations.

Glycidic esters are conventionally synthesized by the Darzens condensation, which however, leads to mixtures of diastereomers. In the direct epoxidation of double bonds with m-chloroperbenzoic acid (MCPBA), on the other hand, the configuration of the olefin is retained in the epoxide formed. Thus we prepared the simple glycidic esters 2a - 2e by refluxing the corresponding α,β-unsaturated esters 1a - 1e with MCPBA in dichloromethane for several days.[1] The reaction proceeded faster with those α,β-unsaturated esters having an α-methyl group (ca. 5d) than with the β-substituted compounds (7 - 11d) or with 1a (13d). The products could easily be isolated by distillation; analytically pure and con-



1 2

	R^1	R^2	R^3
a	H	H	H
b	CH_3	H	H
c	H	CH_3	H
d	CH_3	CH_3	H
e	H	CH_3	CH_3

TABLE: ^{13}C NMR Data [a]

	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	OCH_3
1a	166.5[b] -	128.7 167.5[c]	130.5 161.9				51.5 146.8
1b	167.7 -	136.8 -	125.2 157.2[d] 159.3[d]		18.4 127.9		51.7 146.8
1c	166.8 -	122.8 ~158	144.6 ~153	17.8 127.2			51.2 146.3
1d	168.3 -	128.9 -	136.9 157.1	14.2 126.8	12.0 127.6		51.5 146.3
1e	166.9 -	116.2 159.7	156.4 -	27.2 126.7		20.1 127.5	50.6 145.8
2a	169.9 - e	47.3 186.4 t 2.5[f] H-C(3)	46.3 180.5 d 2.2 H-C(2)				52.4 147.7
2b	171.2 - e	53.6 - t 2.2 H-C(3) q 5.9 H-C(5)	52.9 178.0[d] 178.7[d] q 4.0 H-C(5)		17.5 128.5 d 1.8 H_{cis}-C(3) d 0.9 H_{trans}-C(3)		52.4 147.6
2c	169.7 - e	53.8 184.6 d 1.7 H-C(3) q 4.5 H-C(4)	54.4 177.7 d 2.5 H-C(2) q 5.6 H-C(4)	17.1 127.3 d 6.7 H-C(3) d 2.1 H-C(2)			52.2 147.6
2d	171.8 - q 3.4[g] q 1.8[g] d 3.4[g]	57.3 - d 1.7 H-C(3) q 5.8 H-C(5) q 4.0 H-C(4)	57.8 175.1 q 5.4 H-C(4) q 3.6 H-C(5)	13.4 127.0 d 6.7 H-C(3)	13.3 128.4		52.3 147.4
2e	168.9 - d 5.9 H-C(2) q 3.8 OCH_3	59.2 180.2 q 3.8 H-C(4) q 3.8 H-C(6)	59.9 - d 2.8 H-C(2) q 5.3 H-C(4) q 5.3 H-C(6)	24.2 127.1 d 2.2 H-C(2) q 3.3 H-C(6)		18.3 127.3 q 3.1 H-C(4)	51.9 147.4

a Instrumental parameters: Bruker WH 90 operating at 22.63 MHz; ca 5 M solutions of the esters in $CDCl_3$ with internal TMS; ambient probe temperature; 8k FID's were accumulated, elongated with 8k blanks and the whole transformed to give 8k real spectra. Broad band decoupled spectra: spectral width 6000 Hz; 5 W noise decoupling; flip angle 20°; repetition time 2 s. Proton coupled spectra: spectral width 4000 Hz (for 1a - 1e) or 3000 Hz (for 2a - 2e); 5 W gated noise decoupling; flip 20°; repetition time 5 s. Digital resolution in the transformed spectra: 0.735, 0.488, 0.368 Hz/data point for spectral width of 6000, 4000, 3000 Hz, respectively.

b Chemical shifts in ppm from internal TMS.

c Line separations due to $^1J_{CH}$, in Hz.

d This resonance does not split into a triplet from $^1J_{CH}$ but rather into a doublet of doublets. We cannot see yet, whether the two protons of C(3) show different direct coupling constants, or whether the observed pattern is splitting of higher order due to the strong coupling of the two protons with each other.

e The long-range couplings of these carbonyls were not resolved.

f Line separations due to geminal or vicinal CH coupling, in Hz.

g Tentative assignments.

figurationally uniform (but racemic) products were obtained in 33 - 60 % yield. Whereas the esters 2b - 2e have been previously synthesized by various procedures, compound 2a is - as far as we are aware - described here for the first time.[2)]

Carbon-13 NMR spectra of many epoxides have been recorded and provided valuable data,[3)] however, glycidic esters were not included in these studies. We therefore have measured the carbon-13 NMR spectra of the esters 2a - 2e. The data are compiled in the table together with those of the α,β-unsaturated esters 1a - 1e for comparison.[4)] Chemical shift assignments were in general straightforward. The resonances of C(4) and C(5) in 2d could be identified by specific proton decoupling, and the lines for C(2) and C(3) in 2c were easily distinguished in 2[^{2}H]-2c prepared from methyl 3-hydroxybutyrate via deuteratio in CH_3OD/CH_3ONa, elimination of water with tosyl chloride in pyridine to 2[^{2}H]-1c and epoxidation of the latter with MCPBA.

A comparison of the chemical shifts of the methyl groups in the glycidic esters and the α,β-unsaturated esters shows that in general they differ only by 1 - 2 ppm, 3.0 for C(4) in 1e and 2e being the largest difference measured. However, introduction of an oxygen atom in open chain aliphatic compounds usually deshields the carbons two bonds away by ca. 10 ppm.[5)] Clearly, this rule does not hold for the glycidic esters described in this study. Simple oxiranes, when compared with their parent olefins, show similar trends:[6)] the chemical shifts of the allylic carbons show a striking insensitivity towards epoxidation, a fact which hitherto has not been stressed enough, but will certainly be very useful in the assignment of ^{13}C NMR resonances of epoxides.

CH-coupling constants are further valuable data obtained from ^{13}C NMR spectra. For routine structural investigations the readily available line separations due to the nuclear spin-spin couplings are more suitable than the true coupling constants, which often have to be calculated or must be extracted from simulated spectra. As far as possible, a first order analysis of the fully proton coupled spectra of the esters described here was therefore made and the line separations observed are compiled in the table. The line separations due to one-bond CH-coupling constants show the expected values in both series of compounds. The splittings caused by geminal and vicinal CH-coupling give rise to hardly interpretable patterns in the spectra of the α,β-unsaturated esters, whereas the corresponding splittings in the glycidic esters were more easy to interpret and showed rather constant values throughout the series. The following ranges of line separations were observed for the

different types of couplings in 2a - 2e (see table):

for two-bond couplings:

oxirane C	with oxirane H	:	1.7 - 2.8 Hz
oxirane C	with methyl H	:	5.3 - 5.9 Hz
methyl C	with oxirane H	:	6.7 Hz

for three-bond couplings:

oxirane C	with methyl H	:	3.6 - 4.5 Hz
methyl C	with oxirane H (trans)	:	0 - 0.9 Hz
methyl C	with oxirane H (cis)	:	1.8 - 2.2 Hz
methyl C	with methyl H	:	3.1 - 3.3 Hz

The rather small and non-overlapping ranges observed for the line separations from geminal and vicinal CH-coupling make these splittings valuable tools in the structural analysis of glycidic esters. Geminal couplings seem particularly suitable for the assignment of epoxide carbon resonances, whereas the vicinal couplings can be used for the determination of the oxiran configuration,[7] especially in trisubstituted oxiranes, where the vicinal proton-proton coupling, which otherwise is used for the determination of the oxirane configuration, is absent. On the basis of the abovementioned ranges for the line separations we were recently able to show that the C(14)-C(16) epoxide in the antibiotic hedamycin has the trans configuration.[8]

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REFERENCES AND NOTES

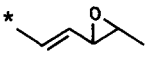
1) V. R. Valente & J. L. Wolfhagen, J. Org. Chem. 31, 2509 (1966).

2) Distilled at 65 - 66.5°/28 torr, bp. 146°/ca.760 torr. ^{1}H NMR ($CDCl_3$, 60 MHz): 3.76 s, 3H, OCH_3; 3.40 br t, 3.5 Hz, 1H, H-C(2); 2.88 d, 3.5 Hz, 2H, H-C(3).

3) cf. e.g. (a) D. R. Paulson, F.Y.N. Tang, G. F. Moran, A. S. Murray, B. P. Pelka & E. M. Vasquez, J. Org. Chem. 40, 184 (1975); (b) S. G. Davies & G. H. Whitham, J.C.S. Perkin II 861 (1975).

4) The chemical shifts of 1a - 1e have been measured previously under different conditions: H. Brouwer & J. B. Stothers, Can. J. Chem. 50, 601 (1972).

5) cf. e.g. E. Pretsch, T. Clerc, J. Seibl & W. Simon, "Tabellen zur Strukturaufklärung organischer Verbindungen mit spektroskopischen Methoden", Springer, Berlin 1976, p. C10.

6) e.g.[3a] 25.5 / 17.1  13.3 vs. 24.1 / 17.9  13.6 and 17.5*  17.7*

7) The usefulnes of vicinal CH-couplings for the determination of configurations in compounds with three-membered rings has recently been pointed out by C. A. Kingsbury, D. L. Durham & R. Hutton, J. Org. Chem. 43, 4696 (1978).

8) Details to be published elsewhere.

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