Tetrahedron Vol. 41, No. 4, pp. 763 to 768, 1985
Printed in Great Britain.

0040-4020/85 $3.00 + .00
Pergamon Press Ltd.

NEW GLYCIDYL ESTER COMPOUNDS CONTAINING A PREFORMED IMIDE RING—I

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(*Received in UK* 17 *October* 1983)

Abstract—The synthesis of the new esterglycidyl compounds produced by condensation of bis-carboxyimides with a large excess of epichlorohydrin were reported. To define the optimal conditions of condensation the process with monofunctional compounds were studied at first. For all synthesis, yield and epoxide and chlorine contents were found. The structure of glycidyl esters was determined by elementary analysis, IR and ^1H and ^{13}C NMR spectra. The physical properties were also defined.

Among epoxy resins, where an oxirane ring is part of the glycidyl group, the following types of epoxides can be distinguished in relation to the nature of the atom to which this group is attached: glycidyl ethers, glycidyl esters, glycidyl amine derivatives. Although the literature concerning esterglycidyl compounds, the products of condensation of carboxylic acid with epichlorohydrin, is in fact substantial,[1-6] however diglycidyl derivatives containing an imide ring have been reported in only a few patents.[7-9]

The purpose of this article is to report the results of the studies on synthesis, structure and physical properties of pure esterglycidyl resins and derivatives of diglycidyl esters prepared from dicarboxylic imide-acids by condensation with epichlorohydrin in a large excess and through their Na salts formed earlier in the reaction of diacids and sodium carbonate in acetone or N,N-dimethylformamide.

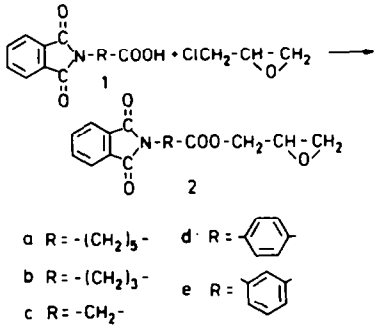
The compounds obtained by these methods were always solid and sparingly soluble, and possessed a little lower epoxide content in comparison with the theoretical calculations.

RESULTS AND DISCUSSION

Prior to the bis-glycidyl derivatives synthesis, five model compounds were prepared by condensation reaction of the epichlorohydrin, generally leads to the formation of α-carboxylic esters of γ-chloropropylene glycol which are then dehydrohalogenated in the presence of strong base to give the desired glycidyl ester. However it has been reported that the glycidyl ester can be obtained directly if epichlorohydrin is in large excess and if a quaternary ammonium halide is used as catalyst.[10] The hydrogen chloride eliminated in the reaction is largely absorbed by the excess epichlorohydrin to form glycerol dichlorohydrin.

We must use this second method to avoid that imide ring in presence of NaOH might be opened and ester group saponified, leading undesired secondary reactions.

Addition of a quaternary ammonium halide was also reported to increase the rate of this reaction. We obtained better results by using benzyl trimethylammonium chloride (BTMA). This reaction is shown in Scheme 1. These model compounds were also used to identify the diglycidyl carboxy derivatives.



The five model compounds were characterized by elemental analysis. IR spectra, ^1H and ^{13}C NMR, m.p. and epoxide equivalent (Table 1). A study more intensive of ^1H and ^{13}C NMR spectra it has been achieved in order to confirm these structures. The ^1H spectra of these glycidyl compounds yield five different signals as it was expected for five protons not equivalent. This unequivalence is due to the presence of an assymetric center and the oxirane ring. These spectra are susceptible to first-order analysis using a 200 MHz spectrometer. In Table 2 the values of the chemical shifts and coupling constants of glycidyl group for all model compounds and also of bis-glycidyl ester derivatives there are listed, and they are in good agreement with the chemical structure.[11-13] The comparison among values of coupling constants allow us to distinguish between protons, of the two methylene groups, in positions *cis* or *trans* referred to central proton (H_c).

Figure 1 shows the spectrum of glycidyl ester of N-(5-carboxypentyl)phthalimide in $CDCl_3$. It contains a complex pattern due to the four aromatic protons (labelled H_o and H_m in Fig. 1) centered at $\delta = 7.8$ ppm and two triplets at $\delta = 3.69$ ppm and $\delta = 2.4$ ppm attributable to methylene groups 1 and 5 respectively. A complex signal to $\delta = 1.68$ (4H) is

Table 1. Model compounds characteristics

Compound	mp (°C)	IR spectra epoxy band (cm^{-1})		Elemental Analysis (%) C	H	N	Cl (%)	E.E (gr/equiv)	yield (%)
2a	36-38	910, 860	calc.	64,35	5,99	4,42	1	350,8	98
			found	63,81	6,00	4,17		(317)	
2b	86-88	910, 860	calc.	62,28	5,19	4,84	1	316	81
			found	62,42	5,38	4,77		(289)	
2c	105-107	910, 860	calc.	59,77	4,21	5,36	0	291	78
			found	60,83	4,34	5,42		(261)	
2d	129-131	910, 830	calc.	66,87	4,02	4,33	1,2	350,6	86
			found	66,28	4,16	4,35		(309)	
2e	164-166	910, 835	calc.	66,87	4,02	4,33	0	340	69
			found	66,84	4,17	4,24		(309)	

2b and 2c were recrystallized from n-heptane, 2d from CCl_4 and 2e from n-butanol

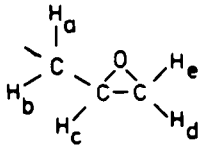
due to the two methylene groups 2 and 4, and the other multiplet centered at $\delta = 1.4$ ppm is attributed to the two protons of the central methylene group.

For the other compounds the following shifts were found: N-(3-carboxypropyl)phthalimide glycidyl ester: 3.77 ppm, t, >N–CH_2–; 2.44 ppm, t, –CH_2–COO–; 2.04 ppm, m, –CH_2–; 7.8 ppm, $H_o + H_m$; N-(carboxymethyl)phthalimide: 4.51 ppm, s, –CH_2– and 7.83 ppm, $H_o + H_m$. In the aromatic compounds **2d** and **2e**, a very complex pattern was observed at the expected region.

The chemical shifts of C atoms are given in Tables 3(a) and 3(b). The resonance lines in each spectrum fall in three areas, 20–70 ppm for the aliphatic carbons, 120–137 ppm for the aromatic carbons and 165–175 ppm for the CO carbons.

In Fig. 2 the spectrum of glycidyl ester of N-(5-carboxypentyl)phthalimide is represented and the same letters and numbers are referred for other ali-

Table 2. Chemical structure and spectroscopic parameters in ^1H NMR of a glycidyl group in model compounds and bis-glycidyl ester derivatives



Compound	Chemical shifts[a] δa	δb	δc	δd	δe	Coupling constants[b] J_{ab}	$J_{bc_{cis}}$	$J_{ac_{trans}}$	J_{de}	$J_{ce_{trans}}$	$J_{cd_{cis}}$
2a	4,41	3,92	3,21	2,84	2,64	12,22	6,24	3,10	4,93	2,62	4,17
2b	4,40	3,92	3,20	2,84	2,64	12,26	6,22	3,10	4,93	2,62	4,17
2c	4,50	4,04	3,23	2,86	2,66	12,19	6,24	3,19	4,79	2,57	4,16
2d	4,68	4,22	3,36	2,92	2,75	12,28	6,19	3,10	4,84	2,61	4,12
2e	4,66	4,22	3,35	2,90	2,73	12,27	6,17	3,21	4,82	2,61	4,14
4a	4,42	3,90	3,20	2,84	2,64	12,37	6,35	2,96	4,86	2,61	4,18
4b	4,33	3,78	3,22	2,77	2,62	12,32	6,54	2,76	5,04	2,65	4,34
4c	4,50	3,94	3,22	2,78	2,65	12,30	6,62	2,54	5,01	2,60	4,30
4e	4,72	4,14	3,35	2,86	2,76	12,42	6,50	2,61	5,01	2,62	4,23

[a]Chemical shifts in ppm from TMS. [b]Coupling constants in Hz

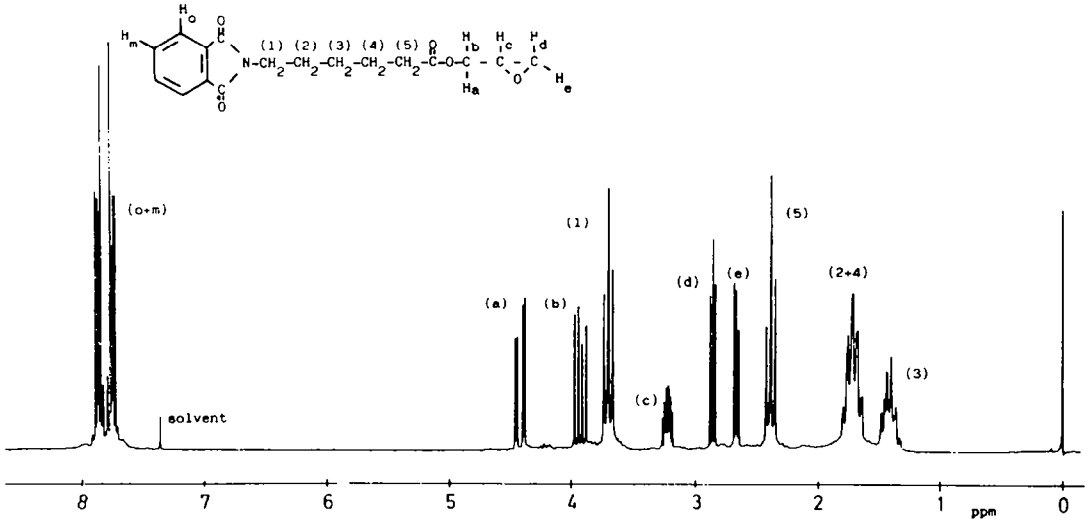
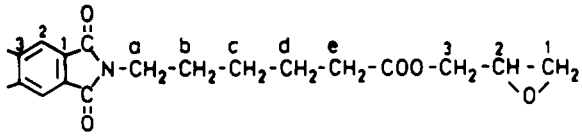


Fig. 1. ^{1}H NMR spectrum of glycidyl ester of N-(5-carboxypentyl)phthalimide in $CDCl_3$.

phatic compounds, whose chemical shifts are listed in Table 3(a). These observed peak shifts are in good agreement with assigned lines on the basis of substituent effect calculations.

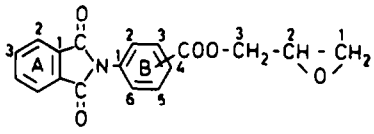
Measurements of the C chemical shifts of the glycidyl group in a large number of ether and amine derivatives have been previously reported.[14] In these compounds the chemical shifts for C–1 falls in the range 43–44.7 ppm and for C–2, 49.1–50.5 ppm. The shifts of C–3 fall in two ranges: 68–73 ppm for glycidyl ethers and 52–56 ppm for glycidyl amines. The shifts of C–1 and C–2 are essentially unaffected

Table 3(a). Chemical shifts of lines observed in the ^{13}C spectra of aliphatic derivatives



	Aliphatic carbons									Aromatic carbons		
	glycidyl carbons			methylene carbons					carbonyl carbons			
	1	2	3	a	b	c	d	e		1	2	3
2a	44,64(t)	49,31(d)	64,80(t)	37,70(t)	28,23(t)	26,29(t)	24,36(t)	33,79(t)	imide 168,01(s) ester 173,10(s)	132,09(s)	123,14(d)	133,84(d)
2b	44,66(t)	49,26(d)	65,02(t)	37,05(t)		23,79(t)		31,24(t)	imide 168,28(s) ester 172,25(s)	132,01(s)	123,23(d)	133,99(d)
2c	44,64(t)	48,98(d)	66,21(t)			38,74(t)			imide 167,26(s) ester 167,51(s)	131,94(s)	123,65(d)	134,31(d)
4a	43,77(t)	48,93(d)	64,57(t)	39,07(t)	27,42(t)	25,58(t)	23,91(t)	33,07(t)	imide 166,27(s) ester 172,53(s)	136,87(s)	117,07(d)	136,87(s)
4b	43,78(t)	48,93(d)	64,75(t)	37,29(t)		23,07(t)		30,63(t)	imide 166,37(s) ester 172,14(s)	136,93(s)	117,02(d)	136,93(s)
4c	43,77(t)	48,73(d)	66,19(t)			39,124(t)			imide 165,33(s) ester 167,11(s)	136,92(s)	118,39(d)	136,92(s)

Table 3(b). Chemical shifts of lines observed in the ^{13}C spectra of aromatic derivatives

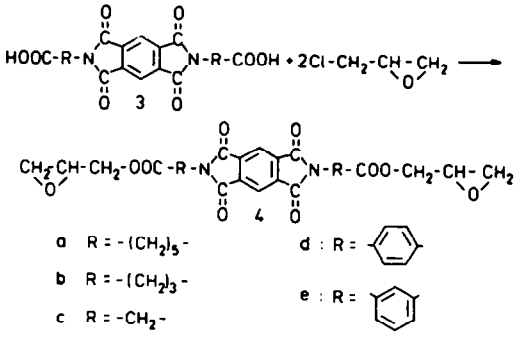


	glycidyl carbons			carbonyl carbons	aromatic carbons								
					ring A			ring B					
	1	2	3		1	2	3	1	2	3	4	5	6
2d	44,62(t)	49,36(d)	65,56(t)	imide 166,38(s) ester 166,64(s)	131,46(s)	125,87(d)	134,62(d)	136,11(s)	123,84(d)	130,47(d)	128,65(s)	130,47(d)	123,84(d)
2e	44,72(t)	49,34(d)	65,73(t)	imide 165,28(s) ester 166,89(s)	131,56(s)	123,80(d)	134,59(d)	132,06(s)	127,82(d)	130,80(s)	129,26(d)	131,20(d)	134,59(d)

by any changes occurring outside of the glycidyl group. But the shift of C–3 is greatly influenced by its neighboring atom (O or N). In our case, glycidyl ester derivatives, the shifts of C–1 and C–2 fall in the referred ranges as it was expected, but the shift of C–3 falls in a different range 64.8–66 ppm because of the presence of an ester group.

As regards diglycidyl ester derivatives, these compounds were obtained by two ways as model compound: using imide-carboxylic acid as initial product or their Na salts, previously obtained in N,N-dimethylformamide, which react with epichlorohydrin as we have described in detail in the Experimental. However the observed yields obtained by the second way were better only in a few cases, owing to the insolubility of the salts.

Reaction conditions found for model compounds were applied to the synthesis of bis-glycidyl derivatives, and a large excess of epichlorohydrin and benzyltrimethylammonium chloride (BTMA) as catalyst was used. The reaction carried out is represented in Scheme 2.



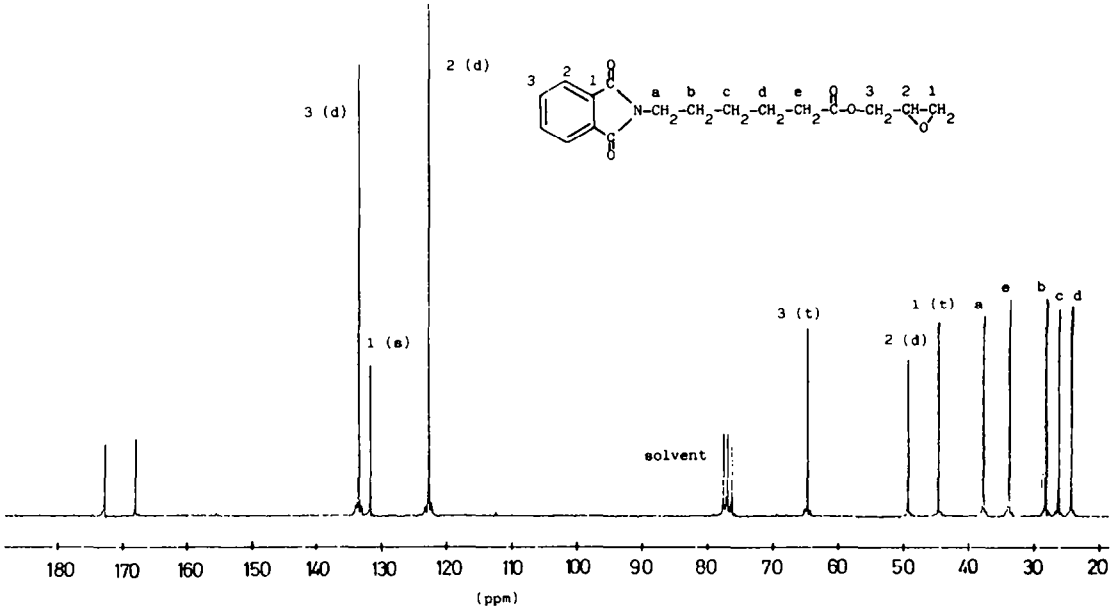


Fig. 2. ^{13}C NMR spectrum of glycidyl ester of N-(5-carboxypentyl)phthalimide in $CDCl_3$.

Table 4. Bis-glycidyl ester characteristics

Compound	mp (°C)	IR spectra epoxy band (cm^{-1})		Elemental Analysis (%) C	H	N	Cl (%)	E.E (gr/equiv)	yield (%)
4a	123-125	907, 855	calc.	60,43	5,75	5,04	1,41	335	96
			found	60,82	5,74	5,00		(278)	
4b	138-139	907, 860	calc.	57,14	4,76	5,55	2,27	310	90
			found	55,55	4,85	5,60		(244)	
4c	201-203	905, 855	calc.	54,05	3,60	6,30	1	270,6	79
			found	53,57	3,57	6,30		(222)	
4d	324	915, 867	calc.	63,38	3,52	4,93	2,76	insol.	82,7
			found	61,24	3,65	4,87			
4e	261-265	910, 830	calc.	63,38	3,52	4,93	2,85	509	77
			found	61,92	3,59	4,83		(284)	

4a was recristallized from ethanol, 4b from toluene and 4c from n-butanol

Characteristic properties of these compounds are collected in Table 4. IR spectra were obtained and characteristic bands of oxirane group were assigned: at 905–915 cm^{-1} (ring deformation).[15,16] At 1700–1750 cm^{-1} CO stretching (imide and ester) was observed and at 725 cm^{-1} a characteristic band of imide group.

These substances follow the general observation that m.p. decrease as the number of aliphatic carbons increases. They were always solid, sparingly soluble, and also followed the general rule that solubility increases with the number of aliphatic carbons. The aromatic compounds were so slightly soluble that it was impossible to obtain ^{13}C NMR spectra and ^{1}H NMR spectrum of *para* derivatives.

The spectral analysis of ^{1}H NMR of all compounds shows an A_2 pattern due to the two equivalent aromatic protons of the pyromellitimide nucleus at δ 8.2–8.4 ppm. The other signals are assigned as follows: N,N'-bis(5-carboxypentyl)pyromellitimide glycidyl ester (**4a**): 3.75 ppm, t, $>N-CH_2-$; 2.37 ppm, t, $-CH_2-COO-$; 1.72 ppm, m, (4H), $-CH_2-$; 1.4 ppm, m, (2H), $-CH_2-$; (**4b**): 3.68 ppm, t, $>N-CH_2-$; 2.46 ppm, t, $-CH_2-COO-$; 1.90 ppm, m, $-CH_2-$; (**4c**): 4.57 ppm, s, $>N-CH_2-COO-$; (**4e**): 8.2–7.7 ppm a complex pattern due to the four protons of the *meta*-substituted ring.

The chemical shifts of the C atoms are collected in Table 3(a). All the results are in good agreement with the ones obtained with model compounds.

EXPERIMENTAL

M.p. are uncorrected and were determined on a Tottoli capillary m.p. apparatus and on a Perkin–Elmer DSC-2. Elemental analysis was carried out on a Perkin–Elmer 240 B device. IR spectra were recorded on a Beckmann model 4260 spectrophotometer (KBr pellet), ^{13}C NMR and ^{1}H NMR spectra ($CDCl_3$ or DMSO) were run on a Varian XL-200 pulsed Fourier transform spectrometer using TMS as the internal standard. Epoxy content was expressed in gram/equivalent and determinated by pyridinium chloride-pyridine method,[17] but bromothymol blue was used as indicator. Cl content was determinated by Schöniger method.

Solvents were purified and dried by standard methods.

Starting materials. Imide-acids **1** and diimide-diacids **3** were obtained in 80–90% yield as described in the lit.[18]

General synthesis of model compounds **2**. The following detailed procedure illustrates the general method used to prepare crude glycidyl esters. A mixture of epichlorohydrin 98 ml (1.25 mole) and N-(3-carboxypropyl)phthalimide 5.825 g (0.025 mole) was heated at 110° and solid benzyltrimethylammonium chloride 0.47 g (0.0025 mole) was added in one batch. The mixture was heated at reflux and the reaction was controlled by TLC ($CHCl_3$/MeOH 99:1), just disappearance of initial product (15 min), was cooled to room temp, and was washed twice with water (25 ml) in a separator funnel. The wash waters were discarded, and unchanged epichlorohydrin was removed from the organic phase by distillation under N_2 and at reduced pressure until the temp of the residue reached 35° at 1 mm. Toluene (50 ml) was added to the residue, and remaining epichlorohydrin was removed as the toluene azeotrope by distillation until the temp of the residue again reached 35° at 1 mm. The properties of **2b** prepared in this way are reported in Table 1.

Synthesis of diglycidyl esters **4**. The followed procedure was similar to the model compound: 78 ml (1 mol) of epichlorohydrin, 3.92 g (0.01 mole) of N,N'-bis(3-carboxypropyl)pyromellitimide and 0.372 g (0.001 mole) of BTMA were mixed. The eluant for TLC was: $CHCl_3$/acetone 1:1.

Acknowledgments—The authors wish to express their appreciation to CIRIT (Comissió interdepartmental de recerca i innovació tecnològica) for providing financial assistance for this work. We also thank Dr. Feliz Ródenas for the provision of NMR spectra.

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