HETEROCYCLES, Vol. 23, No. 12, 1985

REACTION OF DIIMIDE-DIACIDS TRIMELLITIMIDE DERIVATIVES WITH 1-CHLORO-2,3-EPOXYPROPANE

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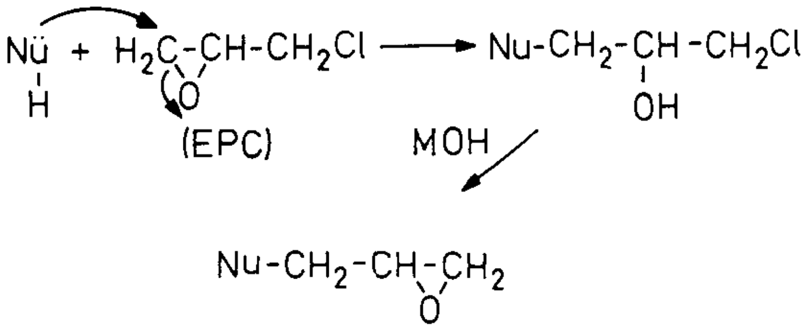
Abstract - The synthesis of various esters containing imide and oxirane cycles has been improved from potassium salts of several diimide-diacids instead of their free carboxylic diacids using 1-chloro-2,3-epoxypropane *in excess* and a quaternary ammonium halide as catalyst. The spectral data and physical and chemical characteristics were discussed.

In this paper we wish to report in detail the convenient way for the synthesis of new oxirane compounds, trimellitimide derivatives.

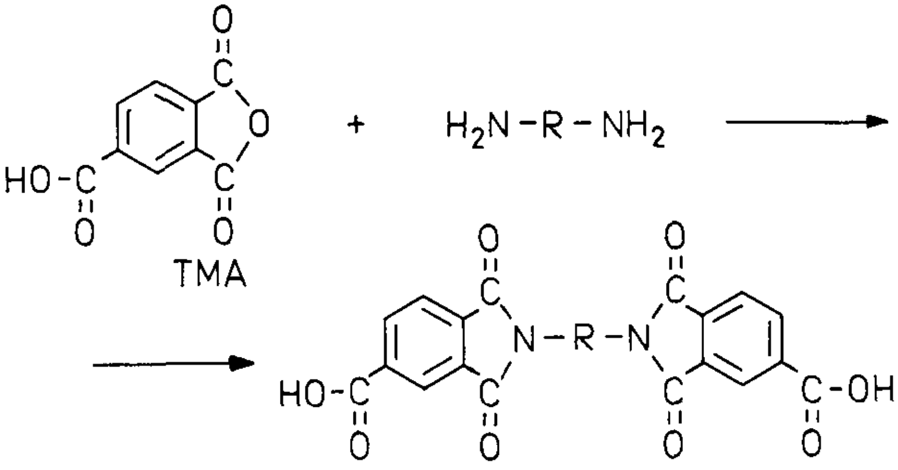
The oxirane ring may be introduced as glycidyl derivative when an epihalohydrin species is used to react with another several functions, such as phenols and alcohols, amines and imides, thiols, and acid groups. These processes usually take place in the presence of alkali, yielding a reaction product consisting mainly of a low molecular glycidyl compound, as it can be seen in the scheme 1:



Scheme 1

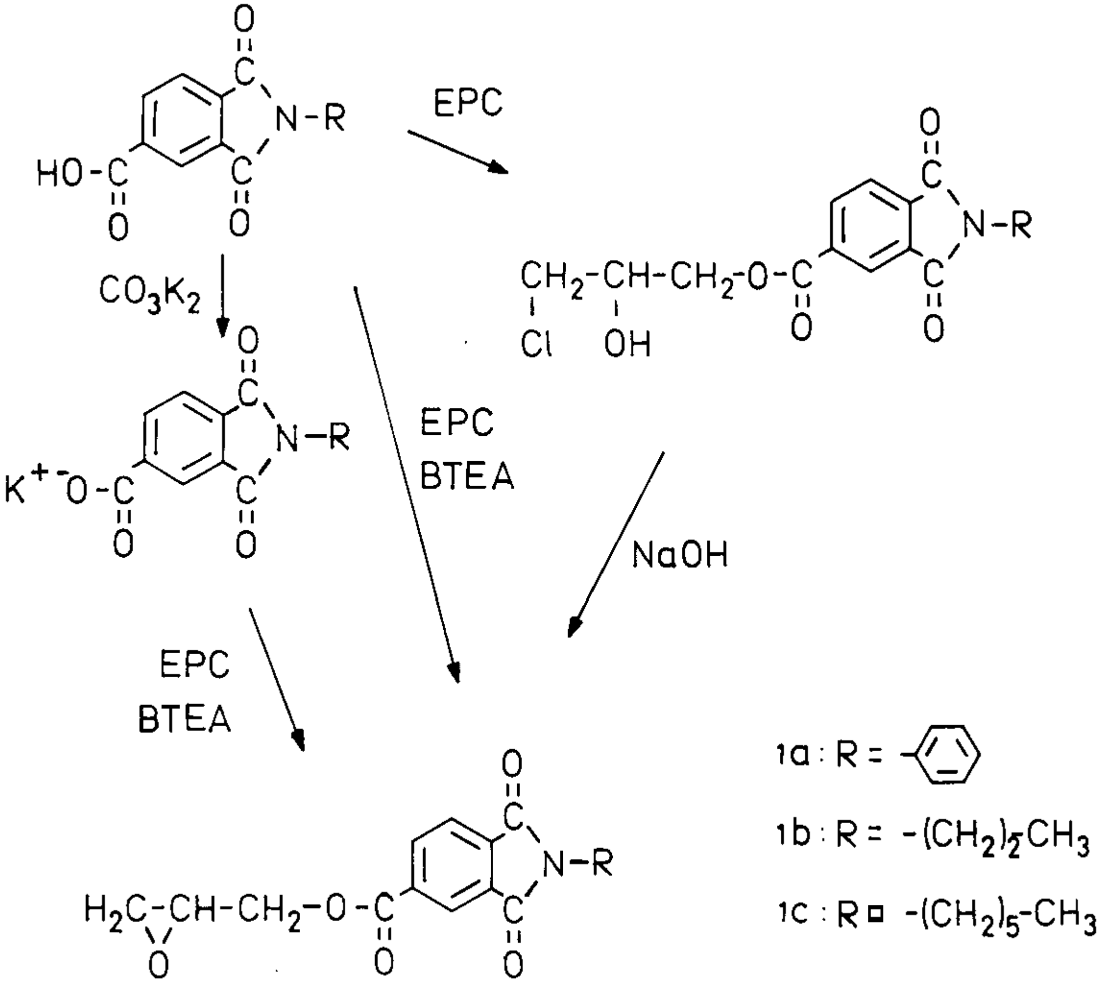
The obtention of glycidyl esters has been widely studied and the number of new formulations as starting products is very high. But although a number of methods for the synthesis of glycidyl esters has been attempted, many of the procedures give the desired product in low yield. In order to overcome this inconvenience the use of alkali as cyclizing agent has been ill-advised by several authors[1], owing to eventual decompositions of ester groups, although very different results were found according to starting products and reaction conditions[2]. Likewise it has been considered that the glycidyl ester group could be obtained directly if 1-chloro-2,3-epoxypropane (epichlorohydrin, EPC) was in large excess and a quaternary ammonium halide was used as catalyst[3]. This technique has been developed to obtain glycidyl ester compounds from several aliphatic and aromatic carboxylic acids, being possible to establish the best reaction conditions in order to achieve good yields of crude residue. Moreover, the use of sodium salts has been reported to increase the purity of the reaction products[1]. Nevertheless, it could be observed that the purity in oxirane ring strongly decreased when dicarboxylic acids or their salts were employed as starting products, although these compounds were aliphatic and linear structures.

In our case, the starting products were diimide-diacids trimellitimide derivatives, whose obtention was carried out as shown in the following scheme:



Scheme 2

As a result of this higher structural complexity, it may be supposed that it is necessary a thorough and systematic study of the best reaction conditions, in order to obtain the products of high epoxy purity. Thus, a previous test with monofunctional derivatives seems desirable and it has been carried out according to the following reactions scheme:



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Scheme 3

As was reported, the treatment of the reaction crude with an inorganic base was reported in several patents[2]. In our case, we have paid attention to the reaction of different reaction crudes with aqueous NaOH (40%). The results which are shown in Table 1, prove the insuitability of this treatment, because the final products have an epoxy content lower than the starting products. The existence of an imide ring group must be probably the principal cause of decreasing in the purity of oxirane ester, as this ring is not stable in basic conditions.

Table 1.- Treatment of the reaction crude of 1a with NaOH.

Initial E.E.[a] (g/equiv)	Molar ratio NaOH:subst.	Time h	Temp. °C	Final E.E. (g/equiv)
513.6	1:1	2	90	734.8
525.0	1:1	2	80	745.0
556.7	1:1	2	80	741.4

[a] Theoretical value for 1a: 323 g/equiv.

Therefore we have tried the employ of a quaternary ammonium halide, namely benzyltriethylammonium chloride (BTEA), as cyclizing agent (see scheme 3), either from the free acids or from their potassium salts. The synthesis of potassium salts was achieved from potassium carbonate better than KOH in avoid to breaking the imide ring, as reported in the experimental part.

The determination of optimum reaction conditions was found to be a very important subject. They were calculated carrying out the process at different times for each sample (see Table 2), and using several quantities of EPC in excess; it could be observed that molar fractions EPC:substract higher than 75:1 gave the best results of yield and epoxy content in the products.

On the other hand, a substancial improvement was achieved when potassium salts were used (Table 3). These results may be explained on the basis of a considerable increase in the nucleophilic character of aromatic carboxy groups when they are converted into their corresponding carboxylate functions. Likewise, no HCl molecules which could react with growing oxirane groups are produced, but potassium chloride is produced and precipitated. The yields, melting points, and physical constants of 1 are summarized in Table 4.

Table 2.- *Reaction of potassium salt of N-phenyltrimellitimide with EPC at different reaction times.*

Time h	Yield %	E.E.[a] (g/equiv)
7	89	614.2
3	92	532.8
1.3	93	497.6
0.7	98	383.2
0.5	96	413.1

[a] Theoretical value for 1a: 323 g/equiv.

Table 3.- Comparison of glycidyl esters from carboxylic acid and its potassium salt.

Compound		Yield (%)	E.E. (g/equiv)	
1a	acid	90	577.6	(323)
	salt	98	383.2	
1b	acid	61	353.2	(289)
	salt	76	298.2	
1c	acid	78	472.4	(331)
	salt	79	345.2	

Table 4.- Characteristics of model compounds.

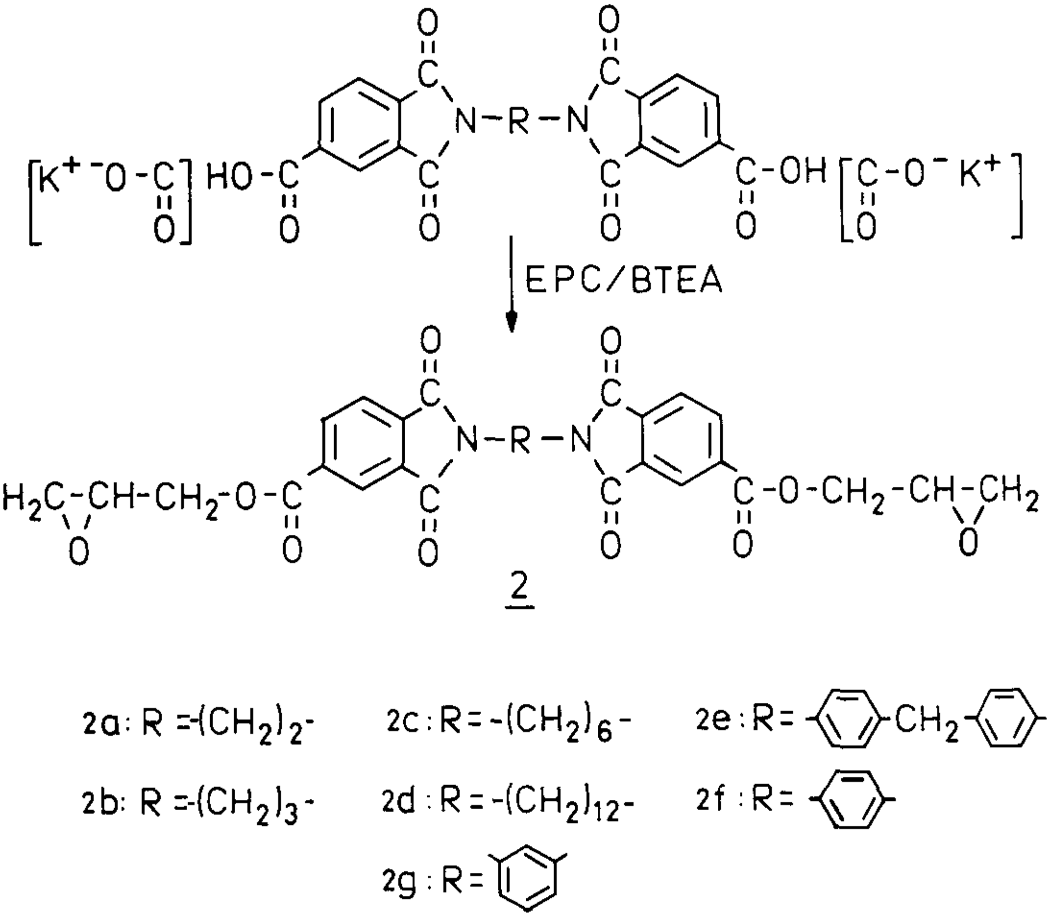
Compound	mp (°C)	IR spectra epoxy band (cm^{-1})		Elemental Analysis (%) C	H	N	Cl (%)
1a*	121-123	900	calc.	66.87	4.02	4.33	1.4
			found	65.95	4.21	4.22	
1b*	49-51	910	calc.	62.28	5.19	4.84	0
			found	60.80	5.10	4.67	
1c*	39-41	910	calc.	65.25	6.34	4.23	0
			found	64.90	6.47	4.04	

* All these products were recrystallized from ethanol.

The synthesis of diglycidyl derivatives was achieved on the basis of the preceding study (see scheme 4). So the reaction conditions described above were applied and the results obtained are shown in Table 5, where it is possible to conclude that free diimide-diacids are not suitable materials as starting products for providing diglycidyl derivatives with high epoxy purity. Nevertheless, their potassium salts gave excellent yields of products with an appropriate purity.

These compounds were characterized as described below for model compounds. All their more important properties are listed in Table 6.

The ir spectra of all compounds showed absorptions due to the oxirane ring deformation (900 cm^{-1}) and no absorption peaks attributed to -OH groups thereby indicating the absence of unreacted halohydrin. The nmr spectral data (H and ^{13}C) also support the structural assignments. The most characteristic feature in the H nmr spectra is the existence of the glycidyl group, which furnishes five groups of signals corresponding to everyone of glycidyl protons; as it was expected, methylene protons are not equivalent owing to the presence of a neighbouring asymmetrical carbon and the rigidity of the epoxy ring[4-5]. All these purposes were confirmed from the ^{13}C nmr data (see Tables 7 a and b).



Scheme 4

EXPERIMENTAL

Melting points were determinated using a Tottoly capillary melting point apparatus and a Perkin-Elmer DSC-2 thermic analyzer, and are uncorrected. The ir spectra were recorded on a Beckmann model 4260 spectrometer (KBr pellet), ^{1}H and ^{13}C nmr spectra were obtained at 200 MHz and 50,3 MHz respectively with a Varian XL-200 pulsed Fourier transform spectrometer using CDCl$_3$ or DMSO-d$_6$ as solvents. The internal standard for nmr spectra was TMS. Elemental analyses were carried out in a Perkin-Elmer 240 B device.

The epoxy content (E.E.) was expressed in g/equivalent and determinated in two ways: pyridinium chloride-pyridine method[6], but bromothymol blue was used as indi-

Table 5.- Comparison of diglycidyl esters from diimide-diacids and their potassium salts.

Compound		Yield %	E.E. (g/equiv)	
2a	acid	91	356.9	(260)
	salt	96	295.3	
2b	acid	90	403.9	(267)
	salt	93	309.1	
2c	acid	93	471.8	(288)
	salt	94	338.7	
2d	acid	92	496.4	(330)
	salt	99	385.7	
2e	acid	67	377.9	(329)
	salt	83	339.3	
2f	acid	70	418.1	(284)
	salt	--*	--	
2g	acid	92	431.8	(284)
	salt	94	401.1	

*Insoluble in EPC.

cator, and Jay-Dijkstra-Dahmen method, variation Ciba[7] Chlorine content was determinated by Schöniger method. Organic solvents were dried and/or distilled as necessary before use. Imide-acids and diimide-diacids were obtained in 80-95% yield as described in the literature[8]. Potassium salts were obtained in acetone, N-methylpyrrolydinone and N,N-dimethylformamide, using equimolecular amounts of starting products and potassium carbonate. For diimide-diacids the use of mechanical stirrer and temperature was necessary.

<u>General synthesis for model compounds</u>. The following detailed procedure illustrates the general method used to prepare crude glycidyl esters. A mixture of EPC and N-propyltrimellitimide or its potassium salt (molar ratio 75:1) was heated and

Table 6.- Diglycidyl esters characteristics.

Compound	mp (°C)	IR spectra epoxy band (cm^{-1})		Elemental Analysis (%) C	H	N	Cl (%)
2a	139-141	900,865	calc.	60.00	3.84	5.38	1.2
			found	59.76	3.89	5.22	
2b	124-127	900,870	calc.	60.67	4.12	5.24	1.5
			found	58.09	4.19	4.98	
2c	132-134	905,870	calc.	62.50	4.86	4.86	1.4
			found	62.01	4.91	4.80	
2d	73*	900,860	calc.	65.45	6.06	4.24	1.7
			found	64.66	6.04	4.24	
2e	254-256	905,860	calc.	67.48	3.95	4.25	0
			found	64.52	4.08	4.01	
2f	> 300	905,835	calc.	63.38	3.52	4.93	3.0
			found	61.93	3.47	4.55	
2g	179-181	900,860	calc.	63.38	3.52	4.93	2.4
			found	61.07	3.53	4.72	

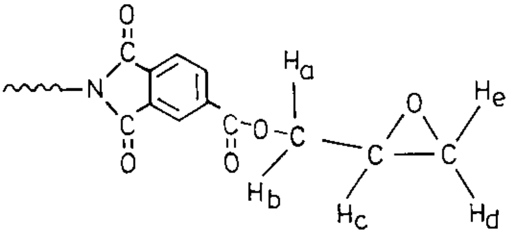
Compounds 2a and 2g were recrystallized from n-butanol, 2c and 2d from ethanol, 2b, 2e and 2f could not be recrystallized.

*Determinated by DSC measurements.

vigorously agitated at 110°C and solid benzyltriethylammonium chloride (BTEA) (0.3 g) (0.0013 mole) was added in a batch. The mixture was heated at reflux for 30 min, cooled to room temperature, and washed twice with water (75 ml) in a separator funnel. The washing waters were discarded, and unchanged epichlorohydrin was removed from the organic phase by distillation under nitrogen and at reduced pressure until the temperature of the residue reached 35°C at 1 mm. Toluene (75 ml) was added to the residue, and remaining epichlorohydrin was removed as the toluene azeotrope by distillation until the temperature of the residue again reached 35°C at 1 mm. The obtained product (1b) was recrystallized from ethanol.

Synthesis of diglycidyl esters (2). The following procedure was similar to the model compounds. Epichlorohydrin was mixed with diimide-diacids or their potassium salts in molar ratio 150:1. The reaction times were between 35-55 min.

Table 7a.- Chemical structure and spectroscopic parameters in ^1H nmr of a glycidyl group in model compounds and diglycidyl ester derivatives.



Compound	Chemical shifts[a]					Coupling constants[b]					
	δ_a	δ_b	δ_c	δ_d	δ_e	J_{ab}	J_{bc}	J_{ac}	J_{de}	J_{cd}	J_{ce}
1a	4.76	4.23	3.39	2.95	2.76	12.3	6.5	3.0	4.6	4.5	2.6
1b	4.76	4.22	3.37	2.94	2.76	12.3	6.5	3.0	4.8	4.1	2.6
1c	4.74	4.22	3.37	2.94	2.76	12.3	6.5	3.0	4.8	4.2	2.6
2a	4.71	4.20	3.35	2.93	2.74	12.3	6.5	2.9	4.6	4.4	2.6
2b	4.73	4.22	3.38	2.94	2.76	12.3	6.4	3.0	4.8	4.2	2.6
2c	4.73	4.22	3.38	2.94	2.76	12.3	6.4	3.0	4.8	4.1	2.6
2d	4.73	4.22	3.38	2.94	2.76	12.3	6.4	2.7	4.5	4.4	2.4
2e	4.74	4.18	--*	2.86	2.77	12.4	6.5	2.7	4.7	4.6	2.6
2f	4.74	4.22	--*	2.94	2.77	12.4	6.5	2.7	4.8	4.6	2.6
2g	4.76	4.24	3.39	2.94	2.77	12.4	6.5	2.7	4.6	4.4	2.6

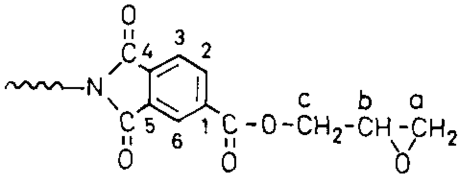
[a] Chemical shifts in ppm from TMS. [b] Coupling constants in Hz.

* This shift remains overlapped by the signal of solvent.

REFERENCES

1. G. Maerker, J.F. Carmichael, and W.S. Port, *J. Org. Chem.*, 1961, **26**, 2681.
2. Ciba-Geigy AG, *Swiss Pat.*, 1974, 1,359,542; *Swiss Pat.*, 1974, 1,363,919.
3. W. Bradley, J. Forrest, and O. Stephenson, *J. Chem. Soc.*, 1951, 1589.
4. W.D. Domke, *Org. Magnetic Res.*, 1982, **18(4)**, 193.
5. D. Gulino, J. Galy, J.P. Pascault, L. Tighzert, and Q.T. Pham, *Makromol. Chem.*, 1983, **184**, 411.

Table 7b.- Chemical shifts of lines observed in the ^{13}C nmr spectra of model compounds and diglycidyl derivatives.



	glycidyl carbons			carbonyl	aromatic carbons					
	a	b	c	carbons	1	2	3	4	5	6
1a	44.7	49.2	66.6	imide 166.2 ester 164.3	135.2	135.9	123.9	135.5	131.3	124.9
1b	44.6	49.1	66.4	imide 167.3 ester 164.3	134.9	135.4	123.2	135.6	132.3	124.2
1c	44.6	49.1	66.4	imide 167.2 ester 164.3	134.9	135.3	123.1	135.7	132.4	124.2
2a	43.9	48.8	66.3	imide 166.8 ester 163.9	134.7	135.4	123.0	134.9	131.8	123.6
2b	44.7	49.2	66.5	imide 167.2 ester 164.4	135.1	135.6	123.4	135.5	132.3	124.5
2c	44.7	49.2	66.4	imide 167.3 ester 164.4	135.0	135.5	123.3	135.7	132.4	124.4
2d	44.7	49.2	66.4	imide 167.3 ester 164.4	135.0	135.4	123.2	135.7	132.4	124.3
2g	44.5	49.0	66.4	imide 165.7 ester 164.1	134.9	135.9	124.9	135.5	131.6	125.4

^{13}C nmr spectra of 2e and 2f have not been done because of the insolubility of these products.

6. B. Dobinson, W. Hofmann, and W.P. Stark, 'The Determination of Epoxide Groups', Pergamon, London, 1969, 1979 Reprinted, p. 18.
7. Idem., p. 40.
8. J. de Abajo, S.G. Babé, and J. Fontán, Ang. Makromol. Chem., 1971, **19**, 121.

Received, 22nd June, 1985