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Acid curing of epoxides: an unexpected mechanism for the reaction of glycidyl esters with acids

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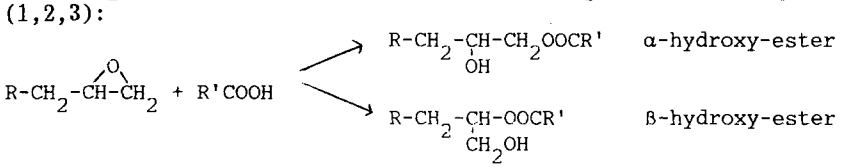
Summary

Products from the reaction of acids with glycidyl esters of other acids were analyzed by ^{13}C-NMR-spectroscopy and HPLC. Besides the two isomeric structures that are normally formed during the ring-opening of epoxides by acids (α- and ß-hydroxy ester), a third structure was observed. This structure was identified by comparative studies as "abnormal" ß-hydroxy ester. A mechanism for the reaction of glycidyl esters with acids is postulated.

Introduction

The ring opening of epoxides by acids usually gives two main products according to which C-atom of the oxirane ring is attacked by the acid (1,2,3):



The ratio of ß to α-isomer depends on the structure of epoxide and acid (4) and on the catalyst used (3). For glycidyl ethers, concentrations of 14-20 % of ß-isomer were found (3), for glycidyl esters of imide acids, the values are in the range of 15-33 % (2).
In addition, several side reactions are observed which include etherification by the reaction of the formed OH-groups with epoxy groups (5) and transesterification of the hydroxy-ester, giving a diol and a diester (5). In this paper results of our studies on the reaction of glycidyl esters with acids are reported. While the reaction of glycidyl esters with its corresponding acids yields the two isomeric α- and ß-hydroxy esters (2), it was found that three main products are formed when an acid reacts with the glycidyl ester of another acid. A possible mechanism for this reaction will be discussed.

Experimental

Hexahydrophthalic diglycidyl ester (HHDGE) was a distilled Ciba-Geigy product with an epoxy content of 6.82 mol/kg (purity 98.5 % by GC). Cyclohexane carboxylic acid glycidyl ester (CHGE) and benzoic acid glycidyl ester (BGE) were prepared as described by Hao and Mleziva (6) and distilled at reduced pressure (purity 98.5 % by GC). Benzyldimethylamine (BDMA) was distilled at reduced pressure (purity > 99.5 % by GC). Dodecanoic acid, cyclohexane carboxylic acid and

benzoic acid were obtained by Fluka (99 %) and used without further purification. For the model reactions, the acid was melted at 130°C in a flask with stirrer and thermometer under nitrogen. Then the catalyst (if any) and the epoxide were added. Samples were taken in regular intervals to determine the epoxy content by titration (with 0.1 N $HClO_4$/acetic acid after addition of tetraethylammonium bromide) and to analyze the products by HPLC.
^{13}C- and ^{1}H-NMR-spectra were recorded on a Bruker SY 100 WP or AM-300 instrument. HPLC-measurements were performed on a Spectra-Physics HPLC-instrument with a UV-detector. Lichrosorb C-18 was used as stationary phase. Eluent was an acetonitrile/water-mixture. A gradient of acetonitrile/water 40:60 to 100 % acetonitrile in 20 min was used for the reaction products of CHGE with dodecanoic acid. Isocratic runs with 55 % acetonitrile/45 % water were applied to separate the products of the reaction of benzoic acid glycidyl ester with dodecanoic acid.

Results

The ^{13}C-NMR spectrum of the reaction product of hexahydrophthalic diglycidyl ester (HHDGE) with dodecanoic acid is shown in fig. 1.

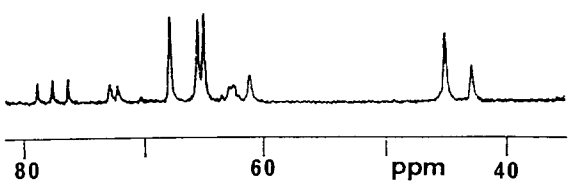
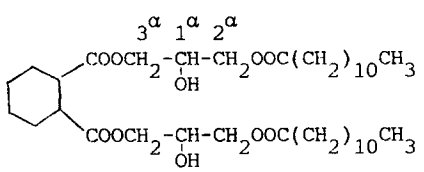


Fig 1 : ^{13}C-NMR-spectrum of the reaction product of HHDGE with dodecanoic acid in $CDCl_3$.

The two peaks at 42.5 (cis) and 45 ppm (trans) indicate that the hexahydrophthalic ester is present in its two isomeric forms (7). From the relative intensities of the two peaks it can be estimated that about 66 % of the trans-form is present, whereas the starting product consisted of 85 % of cis-HHDGE. The three peaks of highest intensity between 60 and 75 ppm can be assigned to the α-hydroxy ester (2,3,8) (fig. 1).



The other peaks at 72, 63 and 61 ppm are normally assigned to the ß-isomer (2,3,8). The spectrum of fig. 1, however, shows two peaks at 72.2 and 72.8 ppm and two overlapping peaks at 62.5 ppm, whereas the spectra found in the literature for the reaction of glycidyl ethers with acids or for diglycidyl esters with their corresponding acids

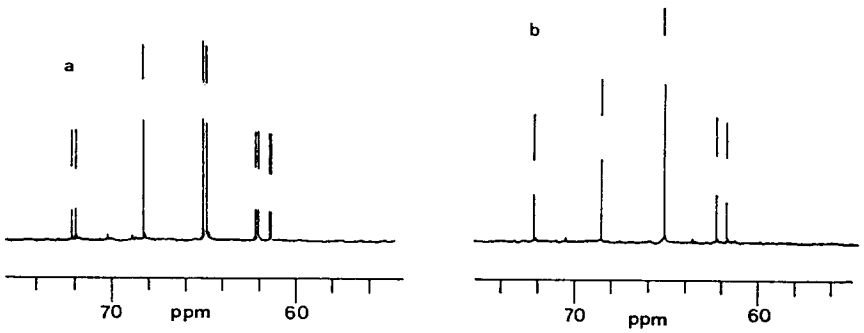


Fig. 2: ^{13}C-NMR-spectra of the reaction products of CHGE with a) dodecanoic acid and b) cyclohexane carboxylic acid

clearly show 1 peak for each of the three carbons of the ß-product (2,3,8). Signals from the side reactions cited above (etherification, transesterification) are normally much smaller and their chemical shifts do not correspond to the additional peaks observed here. Similar spectra were also obtained for the reaction products of HHDGE with other acids.

For further investigations, the monoepoxides cyclohexane carboxylic acid glycidyl ester (CHGE) and benzoic acid glycidyl ester (BGE) were synthesized and reacted with carboxylic acids. The reaction product of CHGE with dodecanoic acid gives a very similar ^{13}C-NMR spectrum as the HHDGE/dodecanoic acid product (fig. 2a). When CHGE reacts with cyclohexane carboxylic acid, however, single peaks are observed at 72, 63 and 61 ppm (fig. 2b), i.e. a very similar spectrum is obtained as reported by Serra et al for the reaction of glycidyl esters of imide acids with **their corresponding** acids (8). HPLC-chromtography shows that three main products (which can hardly be separated) are formed in the first case, but only two products are present in the reaction of CHGE with its corresponding acid (fig. 3a, 3b).

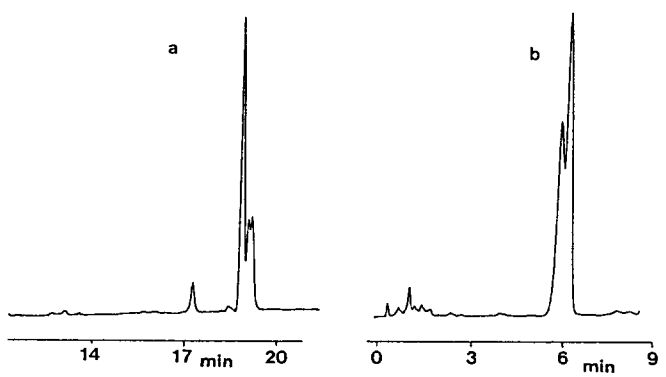
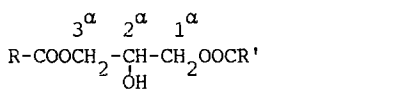
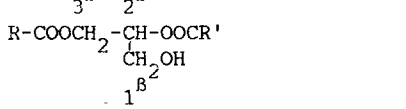


Fig. 3: HPLC-chromatograms of the reaction products of CHGE with a) dodecanoic acid and b) cyclohexane carboxylic acid

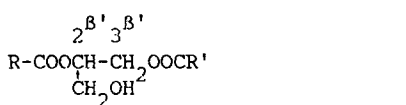
The same is true for the reaction of BGE with acids. The reaction product with dodecanoic acid shows two peaks at 72.4 and 73.3 ppm and at 62.7 and 63.4 ppm. Three reaction products can be separated by HPLC. The reaction of BGE with benzoic acid, however, yields only two reaction products and single peaks at 73.2 and 63.3 ppm are observed. These results can only be explained by assuming that the following three products are formed during the reaction of glycidyl esters with acids.



α-hydroxy ester



ß-hydroxy ester



abnormal ß-hydroxy ester (ß')

R: glycidyl ester rest
R': acid rest

The two ß-products are very similar so that their ^{13}C-NMR-spectra should differ only slightly. In the case of the reaction of a glycidyl ester with its corresponding acid R and R' are identical. Thus ß- and "abnormal" ß-form coincide and only two products can be distinguished, which agrees with the results presented here.
By comparing the spectra of the model reactions, it was tried to make assignments for the different reaction products (table 1).

Table 1 ^{13}C-NMR assignments of α, ß and ß' hydroxy esters (solvent $CDCl_3$)

	δ								
Reaction	1^{α}	3^{α}	2^{α}	1^{β}	3^{β}	2^{β}	$1^{\beta'}$	$3^{\beta'}$	$2^{\beta'}$
CHGE/cyclohexane carboxylic acid	64.99	64.99	68.48	61.62	62.18	72.12			
CHGE/dodecanoic acid	64.77	64.93	68.18	61.31 (?)	62.00	72.11	61.38 (?)	62.15	71.87
HHDGE/dodecanoic acid	64.98	65.52	67.88	61.11	62.9	72.18	61.11	62.55	72.83
BGE/benzoic acid	65.94	65.94	68.13	61.34	63.29	73.21			
BGE/dodecanoic acid	65.26	65.91	68.16	61.35	63.42	72.39	61.35	62.68	73.34

But how can the formation of an "abnormal" ß-product be explained? The first idea could be that an intramolecular transesterification of the α and ß-isomer takes place which could lead to equilibrium concentrations of the three products. Analysis of the products during the reaction shows, that the "abnormal" ß-isomer is formed very quickly from the beginning of the reaction (fig. 4).

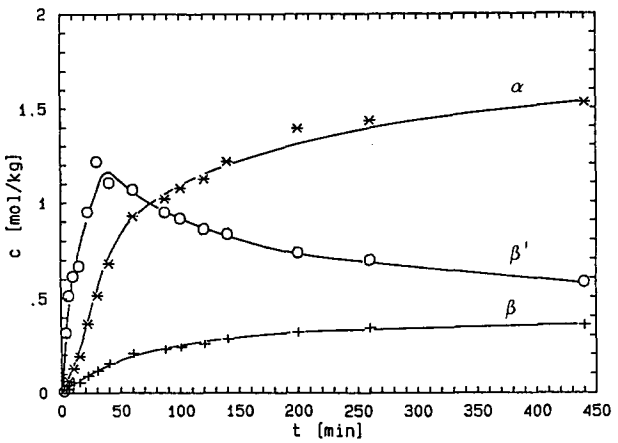


Fig. 4: Kinetics of the formation of α, ß and ß'-hydroxy ester from BGE and dodecanoic acid

A transesterification is, however, only possible when some α- and ß-hydroxy ester is already formed and it should be accelerated with increasing concentration of hydroxyl containing products. But it can be assumed that the carboxyl group plays an important role as a sort of neighbouring group in the reaction. The high acid concentration in the reaction mixture leads to the formation of the conjugated acid of the epoxide. In this form, the C-atoms (especially the secondary C-atom) of the oxirane ring carry a partial positive charge. An interaction of the carboxyl group with either of these activated C-atoms may give two different intermediates, a 6-membered and a 5-membered ring (fig. 5). In the case of the aliphatic glycidyl ester, the intermediates can be stabilized by the abstraction of a proton (catalyzed by a base or a carboxylate ion), thus forming a double bond adjacent to the cyclohexane ring. Evidence for the presence of such a double bond is given by the cis-trans isomerization observed during the reaction of HHDGE with acids. The aromatic glycidyl ester can stabilize the positive charge by delocalization in the ring. Addition of a carboxylate ion can then occur at carbon atom 1 or 2 of the intermediate. In the case of the 6-membered ring, reaction at either of the C-atoms yields the same product, the α-hydroxy ester. Attack at C-atom 1 of the 5-membered ring gives the "normal" ß-product attack at C-atom 2 the "abnormal" ß-product. The postulated reaction sequence is shown in fig. 5.
The preferred formation of the abnormal ß-product at the beginning of the reaction (fig. 4) is plausible because the secondary C-atom of the oxirane ring can better stabilize the positive charge. This favors a

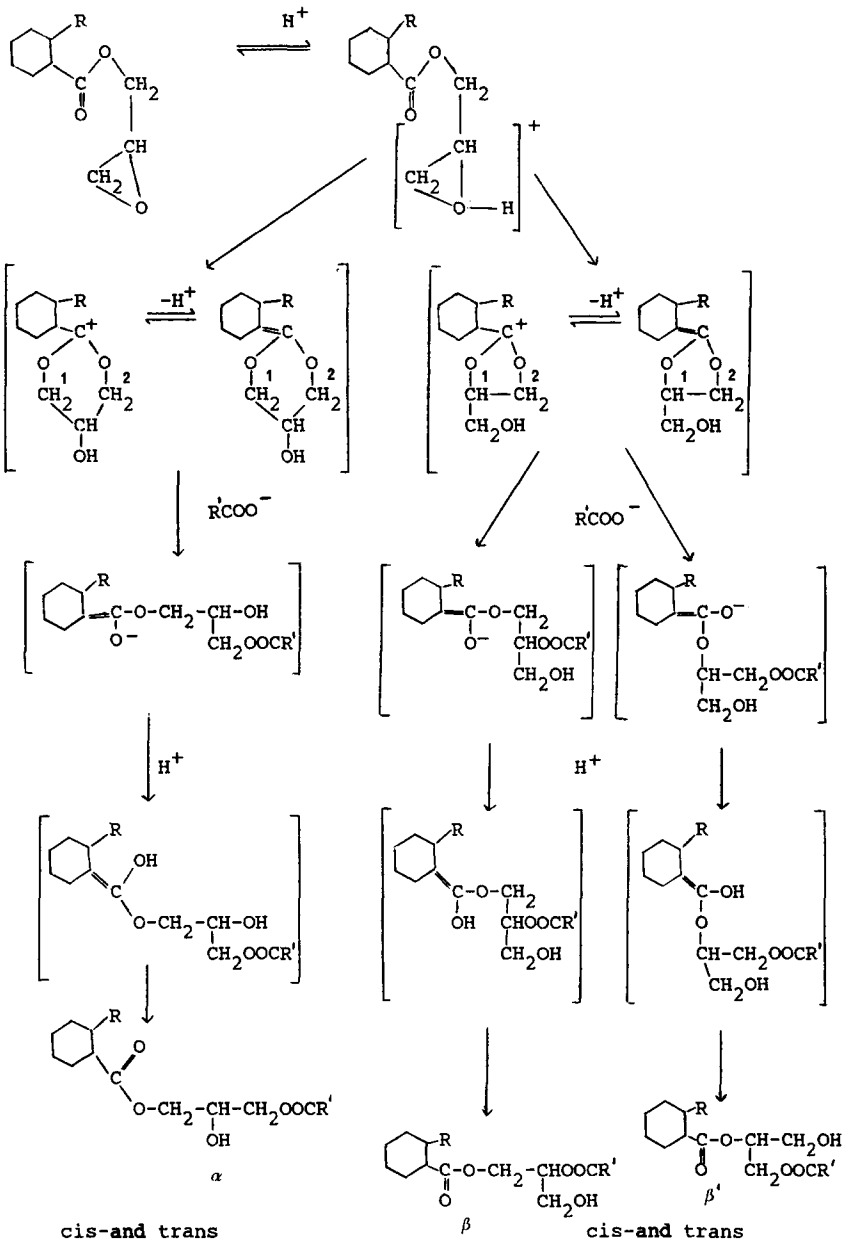
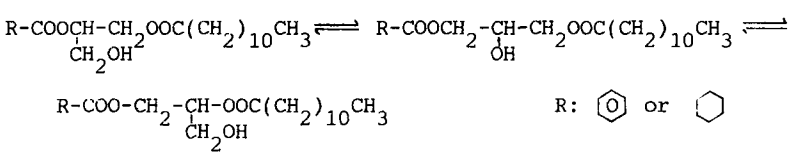


Fig. 5: Postulated mechanism for the reaction of glycidyl esters with acids

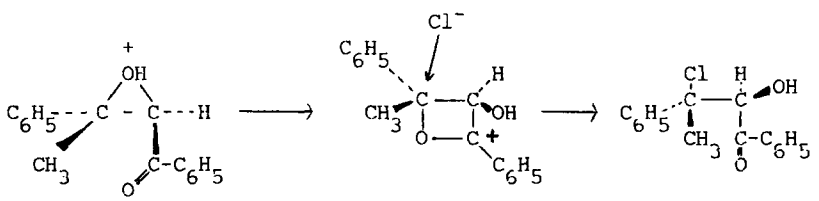
rapid interaction with the carboxyl group, leading to the 5-membered ring as intermediate. Attack of the acid must then be faster at the primary C-atom because of sterical reasons. In the course of the reaction, formation of the α-isomer becomes, however, dominant. It is possible that the formation of the 6-membered ring (although slower) is formed in higher concentrations because of its higher stability, thus giving more α-isomer. Or it could be conceivable that, as a parallel reaction, direct attack of the acid occurs at the oxirane ring without the cyclic intermediate. This favors the formation of the α-isomer (besides some ß-isomer), but does not yield the ß'-isomer. It is, however, not probable, that only the ß-isomer is formed via the cyclic intermediate, whereas the "normal" α and ß-hydroxy esters would exclusively be products of the normal ring opening of the epoxide by direct attack of the acid. In the case of the 1,2-disubstituted epoxide HHDGE more than 50 % conversion to the trans-form is observed, which is even more than the sum of ß **and** ß'-concentrations (30 %).

At about 60-65 % conversion of epoxy groups, the concentration of the ß-product reaches a maximum, after which it decreases slowly (fig. 4). Similar kinetics (but with a less marked maximum) were observed for the aliphatic CHGE/dodecanoic acid system. These results indicate, that, as a side reaction, transesterification takes place, leading to an equilibrium between the three products:



Thus, two effects, the mechanism involving an interaction of the carbonyl group with the epoxide, forming cyclic intermediates **and** the subsequent transesterification lead to the final distribution of the three isomeric products.

A similar mechanism, involving a carbonyl as neighbouring group in an epoxide reaction, was postulated by Wasserman and Aubrey (9) to explain the ring opening of certain epoxides giving retention of configuration:



Conclusions

A new mechanism has been found for the reaction of glycidyl esters with acids which involves the carbonyl of the glycidyl ester as neighbouring group. In our opinion, this mechanism gives a satisfactory explanation for both effects observed during the reaction of glycidyl esters with acids, i.e. the formation of an abnormal ß-product **and** the cis-trans isomerization of the 1,2-disubstituted cyclohexane derivative.

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