Spectroscopical contributions to the regioselectivity of nucleophilic curing reactions in epoxy resins

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The point of nucleophilic attack in epoxy resins have been studied using monofunctional epoxides and amines. These model reaction systems allow analytical and preparative separations of reaction products formed. Thus these reaction products can be characterized and analysed by mass and NMR spectroscopical methods. The results from these investigations show that the terminal carbon atom of the cyclic three-membered ring is attacked selectively by nucleophilic agents such as amines forming corresponding β-aminoalcohols. Therefore, the formation of polymers containing primary β-aminoalcohol structures have to be excluded.

Key words: epoxides; model reactions; β-aminoalcohols; mass spectroscopy; ^{1}H NMR and ^{13}C NMR spectroscopy

Epoxy-based adhesives are, today, one of the most important types of structural adhesive[1]. As by a polyaddition curing adhesive they are comparatively simple in handling and application. This is due to the exceptional reactivity of the epoxy group. The cyclic three-membered ring is extremely strained (see Fig. 1). Furthermore both carbon atoms are partially positively charged due to the electron-withdrawing effect of the oxygen atom[2].

In acidic curing systems the regioselectivity of epoxy openings is governed by the higher stability of the competitive carbonium ions formed. Therefore, two competitive reactions forming primary and secondary alcohols are well known[2,3]. In principle, similar competitive reactions may occur in nucleophilic systems. Both positively charged carbon atoms in the epoxy ring can be attacked by nucleophilic agents such as amines. Such a nucleophilic attack should be preferred at this point due to lower sterical hindrance at the terminal carbon atom. If this sterical effect is negligible, two competitive reactions forming primary and secondary β-aminoalcohols may be possible. However, the curing can be followed by formation of chemical inhomogeneous polymers containing different molecular structures (see Fig. 2).

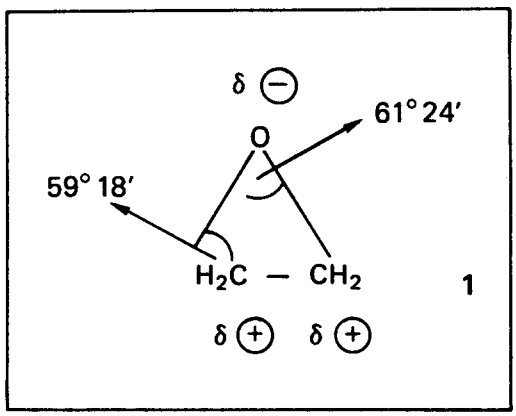

Fig. 1 Epoxy ring in ethylene oxide (1)

Procedure

Investigations on this problem are mainly based on IR-spectroscopy[3] which in this instance is less informative. Generally[4-6], only the reaction mechanism and the reaction products are formulated (see Fig. 3). This reaction behaviour, in which all curing reactions occur via additions of amino groups of the hardeners onto epoxy groups at the same point of attack, is the central problem investigated in this paper.

Without chemical decomposition the polymers

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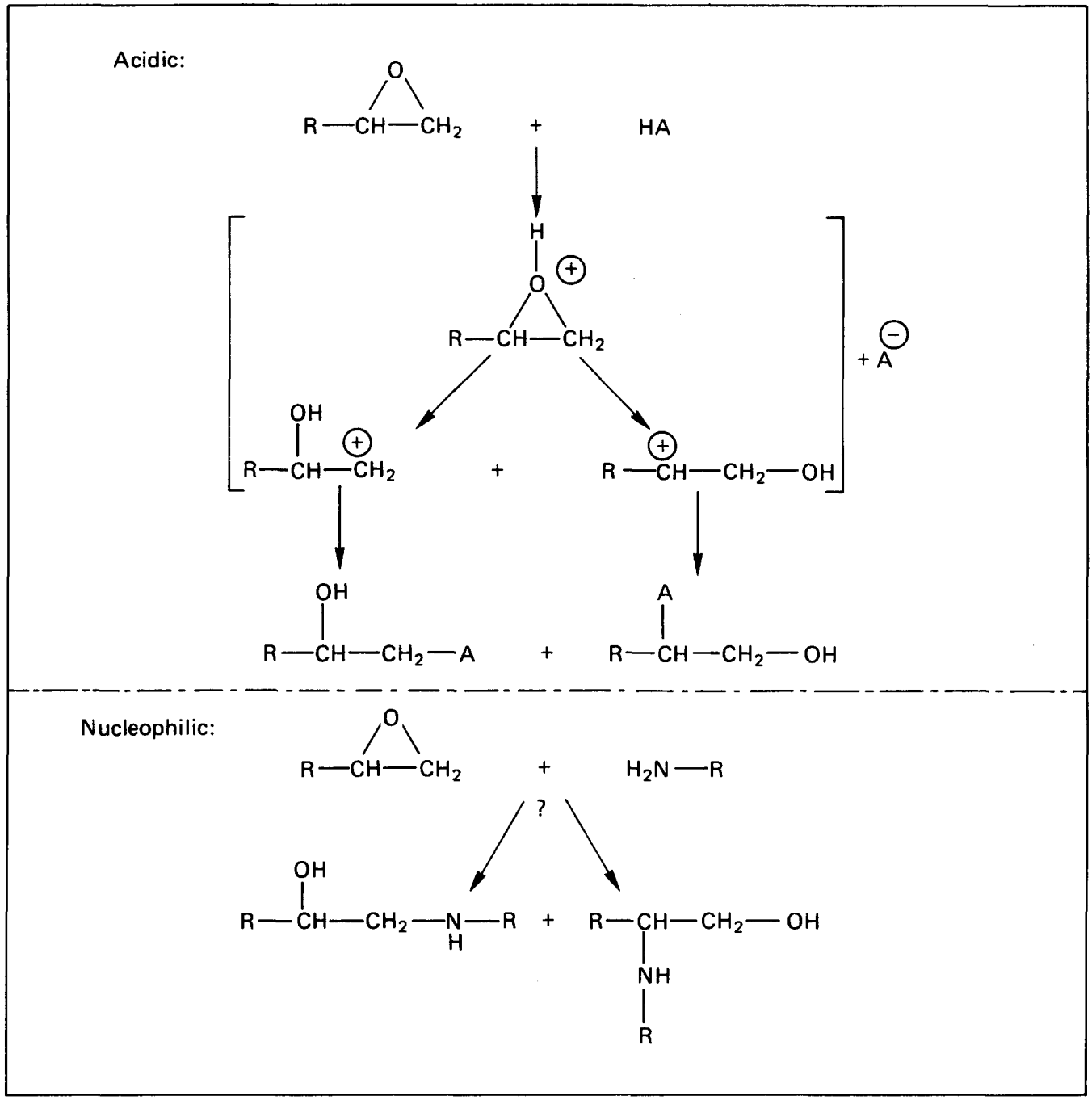

Fig. 2 Competitive reactions in acidic and nucleophilic systems

formed in the curing can hardly be analysed by physical or chemical methods. For this reason a model reaction system was chosen. Its components are functionally similar to technical analogues, but they cannot polymerize. Therefore investigations like mass, ^{1}H NMR and ^{13}C NMR spectroscopic analyses at monomeric reaction products become possible. The model epoxide 1,2-epoxy-3-(4-methyl-phenoxy)-propane (6) has been described[7] and is subsequently referred to as monoepoxide. These studies are supported by similar investigations on propylene oxide (7) reaction products (see Fig. 4).

The reaction products of monofunctional epoxides (6, 7) and amines are β-aminoalcohols. Spectroscopic investigations based on nucleophilic attack consideration products of monoepoxide (6) and primary amines (see Fig. 5) give unequivocal results.

Experimental details

Analytical techniques

The monofunctional epoxides (6, 7) and amines in a variety of molar ratios were stirred at room temperature. The reactions were complete when all the epoxide has reacted. This could be controlled with thin layer chromatography (TLC) on aluminium sheets coated with silica gel 60 F_{254} (layer thickness 0.2 mm, from Merck) with a toluene/acetonitrile mobile solvent at a ratio of 2:1. All analytical data were obtained from the

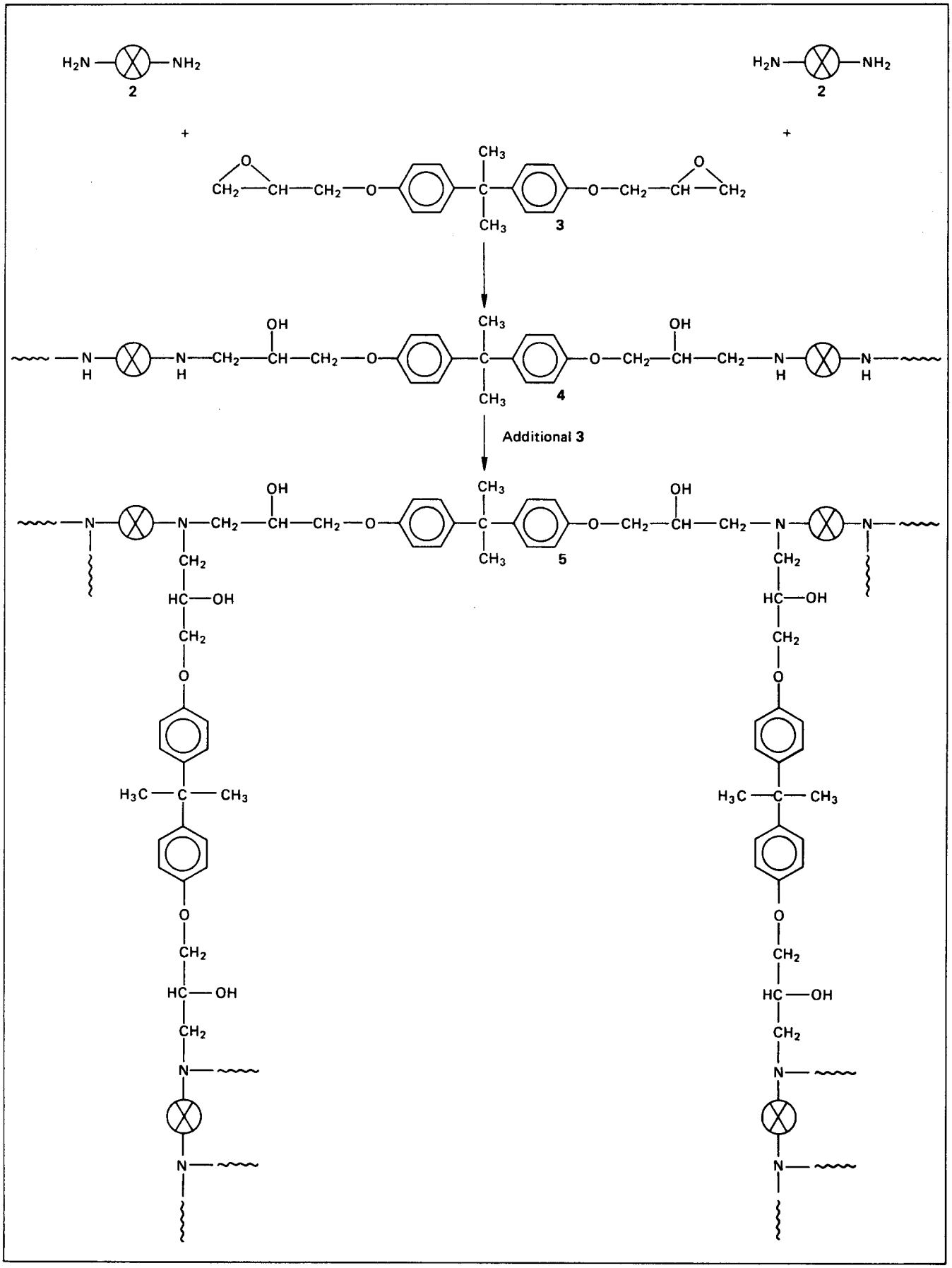

Fig. 3 General reaction mechanism

Table 1. β-aminoalcohols from monoepoxode (6)

N-[3-(4-methyl-phenoxy)-2-hydroxy-propyl-1]-propyl amine (propyl amine-monoadduct) **(8)**

N,N-di-[3-(4-methyl-phenoxy)-2-hydroxy-propyl-1]-propyl amine (propyl amine-diadduct) **(9)**

N-[3-(4-methyl-phenoxy)-2-hydroxy-propyl-1]-dipropyl amine (dipropyl amine-adduct) **(10)**

from monoepoxide (**6**) and propyl amine **(8, 9)**

resp. monoepoxide (**6**) and dipropyl amine in molar ratio: **(10)**

1:1 (**8**); 2:1 (**9**), 1:1 **(10)**

Molecular weight:
223.32 g mol^{-1} (**8**); 387.52 g mol^{-1} (**9**); 265.4 g mol^{-1} **(10)**

Elemental analyses:

	(8)		(9)		(10)	
	calc	found	calc	found	calc	found
C:	69.92	69.84	71.19	71.38	72.41	72.32
H:	9.48	9.41	8.58	8.72	10.25	10.33
N:	6.27	6.21	3.61	3.55	5.27	5.20

N-[3-(4-methyl-phenoxy)-2-hydroxy-propyl-1]-aniline (aniline-monoadduct) **(12)**

N,N-di-[3-(4-methyl-phenoxy)-2-hydroxy-propyl-1]-aniline (aniline-diadduct) **(13)**

from monoepoxide (**6**) and aniline in molar ratio:
1:1 (**12**); 2:1 (**13**)

Molecular weight: 257.33 g mol^{-1} (**12**); 421.54 g mol^{-1} (**13**)

Elemental analyses:

	(12)		(13)	
	calc	found	calc	found
C:	74.69	74.59	74.08	74.02
H:	7.44	7.52	7.41	7.33
N:	5.44	5.39	3.32	3.11

N-[3-(4-methyl-phenoxy)-2-hydroxy-propyl-1]-^{tert}butyl amine (^{tert}butyl amine-monoadduct) **(14)**

N,N-di-[3-(4-methyl-phenoxy)-2-hydroxy-propyl-1]-^{tert}butyl amine (^{tert}butyl amine-diadduct) **(15)**

N-[3-(4-methyl-phenoxy)-2-hydroxy-propyl-1]-diisopropyl amine (diisopropyl amine-adduct) **(11)**

from monoepoxide (**6**) and ^{tert}butyl amine **(14, 15)**

resp. monoepoxide (**6**) and diisopropyl amine **(11)**
in molar ratio:
1:1 (**14**); 2:1 (**15**); 1:20* (**11**)

Molecular weight:
237.34 g mol^{-1} (**14**); 401.55 g mol^{-1} (**15**); 265.4 g mol^{-1} (**11**)

Elemental analyses:

	(14)		(15)		(11)	
	calc	found	calc	found	calc	found
C:	70.85	70.73	71.79	71.71	72.41	72.30
H:	9.77	9.86	8.79	8.84	10.25	10.39
N:	5.90	5.79	3.49	3.56	5.28	5.36

N-[3-(4-methyl-phenoxy)-2-hydroxy-1]-dimethyl amine (dimethyl amine-adduct) **(16)**

N-[3-(4-methyl-phenoxy)-2-hydroxy-1]-piperidine (piperidine-adduct) **(17)**

from monoepoxide (**6**) and dimethyl amine* **(16)**

resp. monoepoxide (**6**) and piperidine **(17)**
in molar ratio:

dimethyl amine excess* (**16**): 1:1 (**17**)

Molecular weight:
209.29 g mol^{-1} (**16**); 249.35 g mol^{-1} (**17**)

Elemental analyses:

	(16)		(17)	
	calc	found	calc	found
C:	68.69	68.60	72.25	72.37
H:	9.15	9.22	9.30	9.41
N:	6.69	6.58	5.62	5.50

*Reflux.

reaction products without any purification as the results show that there was no need. Data from elemental analyses (Tables 1 and 2), obtained on a Perkin-Elmer elemental analyser 240, are expressed in percent of molecular weight. Mass spectra were recorded on a Varian MAT 331 A instrument. From each mass spectrum (70 eV) important peaks and their relative intensity in percent are given (Table 3). ^{1}H NMR spectra were recorded on a Bruker WP 80 DS instrument at 80 MHz (Table 4), ^{13}C NMR spectra on a Bruker 300 MHz spectrometer AM 300 at 75.5 MHz (Table 5). The reaction products were dissolved in deuterated trichloromethane ($CDCl_3$) containing 1% trimethyl silane (TMS). All absorptions are given as

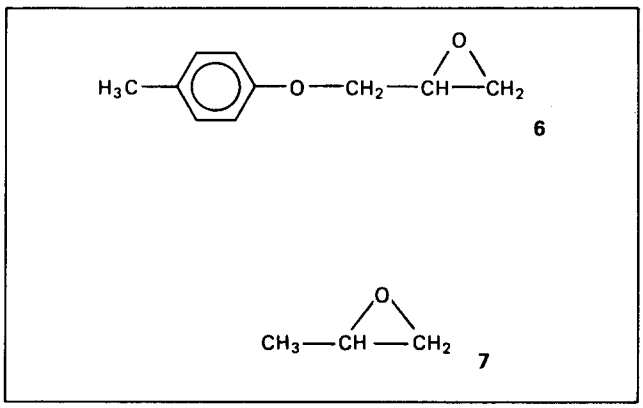

Fig. 4 Monoepoxide (**6**) and propylene oxide (**7**)

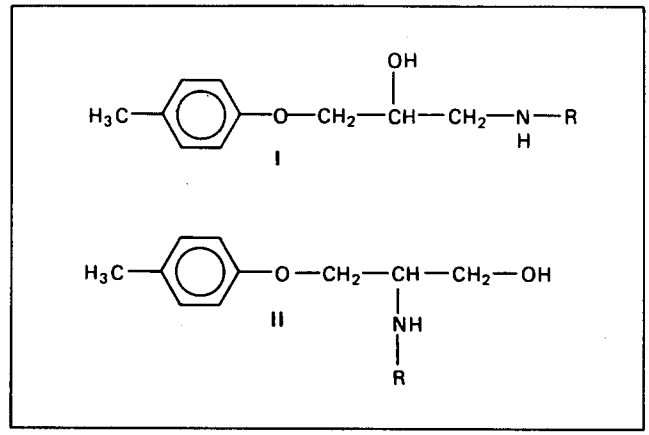

Fig. 5 Competitive β-aminoalcohols I, II on branch of monoepoxide (**6**)

Table 2. β-aminoalcohols from propylene oxide (7)

N-(2-hydroxy-propyl-1)-propyl amine (propyl amine-monoadduct) **(18)**

N,N-di-(2-hydroxy-propyl-1)-propyl amine (propyl amine-diadduct) **(19)**

N-(2-hydroxy-propyl-1)-diisopropyl amine (diisopropyl amine-adduct) **(20)**

from propylene oxide (**7**) and propyl amine **(18, 19)**

resp. propylene oxide (**7**) and diisopropyl amine (**20**)* in molar ratio:

1:1 (**18**); 1:1 (**19**), 1:1 (**20**)*

Molecular weight:
117.19 g mol^{-1} (**18**); 175.27 g mol^{-1} (**19**); 159.27 g mol^{-1} (**20**)

Elemental analyses:

	(18)		(19)		(20)	
	calc	found	calc	found	calc	found
C:	61.49	61.58	54.82	54.60	67.87	67.78
H:	12.90	12.79	12.08	12.15	13.29	13.35
N:	11.95	11.82	7.99	8.11	8.79	8.89

N-(2-hydroxy-propyl-1)-aniline (aniline-monoadduct) **(21)**

N,N-di-(2-hydroxy-propyl-1)-aniline (aniline-diadduct) **(22)**

N-methyl-N-(2-hydroxy-propyl-1)-aniline (N-methylaniline-adduct) **(23)**

from propylene oxide (**7**) and aniline **(21, 22)**

resp. propylene oxide (**7**) and N-methylaniline **(23)**
in molar ratio:

1:1 (**21**); 2:1 (**22**); 1:1 (**23**)

Molecular weight:
151.21 g mol^{-1} (**21**); 209.29 g mol^{-1} (**22**); 165.24 g mol^{-1} (**23**)

Elemental analyses:

	(21)		(22)		(23)	
	calc	found	calc	found	calc	found
C:	71.49	71.41	68.87	68.98	72.69	72.58
H:	8.67	8.53	9.15	9.08	9.15	9.31
N:	9.26	9.38	6.69	6.75	8.48	8.31

*Reflux.

Table 3. Complete mass spectroscopic data

	(8)			**(9)**	
$M^{+\cdot}$	223	(2)	$M^{+\cdot}$	387	(1)
$(M-C_2H_5)^{+\cdot}$	194	(1)	$(M-C_2H_5)^{+\cdot}$	358	(1)
$(M-C_2H_4O)^{+\cdot}$	179	(8)	$(M-C_9H_{11}O_2)^{+\cdot}$	236	(100)
$(M-C_9H_{11}O_2)^{+\cdot}$	72	(100)	$(M-C_{18}H_{21}O_4)^{+\cdot}$	86	(46)
	(10)				
$M^{+\cdot}$	265	(2)			
$(M-C_2H_5)^{+\cdot}$	236	(3)			
$(M-C_9H_{11}O_2)^{+\cdot}$	114	(100)			
	(12)			**(13)**	
$M^{+\cdot}$	257	(12)	$M^{+\cdot}$	421	(16)
$(M-C_2H_4O)^{+\cdot}$	213	(1)	$(M-C_9H_{11}O_2)^{+\cdot}$	270	(100)
$(M-C_9H_{11}O_2)^{+\cdot}$	106	(100)	$(M-C_{18}H_{21}O_4)^{+\cdot}$	120	(83)
	(14)			**(15)**	
$M^{+\cdot}$	237	(3)	$M^{+\cdot}$	401	(1)
$(M-CH_3)^{+\cdot}$	222	(17)	$(M-CH_3)^{+}$	386	(4)
$(M-C_2H_4O)^{+\cdot}$	193	(9)	$(M-C_4H_9)^{+\cdot}$	344	(1)
$(M-C_9H_{11}O_2)^{+\cdot}$	86	(69)	$(M-C_9H_{11}O_2)^{+\cdot}$	250	(89)
$(M-207)^{+\cdot}$	30	(100)	$(M-C_{13}H_{19}O_2)^{+\cdot}$	194	(47)
			$(M-C_{18}H_{21}O_4)^{+\cdot}$	100	(1)
			$(M-C_{20}H_{26}NO_4)^{+\cdot}$	57	(19)
			$(M-357)^{+\cdot}$	44	(100)
	(11)				
$M^{+\cdot}$	265	(2)			
$(M-CH_3)^{+\cdot}$	250	(2)			
$(M-C_8H_9O)^{+\cdot}$	144	(3)			
$(M-C_9H_{11}O_2)^{+\cdot}$	114	(100)			
	(16)			**(17)**	
$M^{+\cdot}$	209	(4)	$M^{+\cdot}$	249	(3)
$(M-H_2O)^{+\cdot}$	191	(1)	$(M-C_8H_9O)^{+\cdot}$	128	(3)
$(M-C_8H_9O)^{+\cdot}$	88	(2)	$(M-C_9H_{11}O_2)^{+\cdot}$	98	(100)
$(M-C_9H_{11}O_2)^{+\cdot}$	58	(100)			
	(18)			**(19)**	
$M^{+\cdot}$	117	(3)	$M^{+\cdot}$	175	(1)
$(M-CH_3)^{+\cdot}$	102	(5)	$(M-CH_3)^{+\cdot}$	160	(3)
$(M-C_2H_5)^{+\cdot}$	88	(8)	$(M-C_2H_5)^{+\cdot}$	146	(2)
$(M-C_2H_5O)^{+\cdot}$	72	(100)	$(M-C_2H_5O)^{+\cdot}$	130	(100)
$(M-C_3H_9N)^{+\cdot}$	58	(6)	$(130-C_3H_6O)^{+\cdot}$	72	(19)
	(20)				
$M^{+\cdot}$	159	(4)			
$(M-CH_3)^{+\cdot}$	144	(10)			
$(M-C_3H_7)^{+\cdot}$	116	(3)			
$(M-C_2H_5O)^{+\cdot}$	114	(100)			
$(114-C_3H_6O)^{+\cdot}$	56	(15)			
	(21)			**(22)**	
$M^{+\cdot}$	151	(16)	$M^{+\cdot}$	209	(11)
$(M-C_2H_5O)^{+\cdot}$	106	(100)	$(M-C_2H_5O)^{+\cdot}$	164	(100)
$(M-C_3H_6O)^{+\cdot}$	93	(6)	$(M-C_3H_6O)^{+\cdot}$	106	(59)
$(M-C_3H_8NO)^{+\cdot}$	77	(21)			
	(23)				
$M^{+\cdot}$	165	(47)			
$(M-CH_3)^{+\cdot}$	150	(4)			
$(M-C_2H_5O)^{+\cdot}$	120	(100)			
$(M-C_3H_7O)^{+\cdot}$	106	(25)			
$(M-C_3H_8O)^{+\cdot}$	105	(45)			
$(M-C_3H_9O)^{+\cdot}$	104	(46)			
$(M-C_4H_{10}NO)^{+\cdot}$	77	(54)			

Values given in parentheses are relative intensity (%), (70 eV, m z^{-1})

Table 4. Complete ^{1}H NMR spectroscopic data

	$CDCl_3$, TMS;	δ (ppm) [80 MHz]		
		(8)	**(9)**	**(10)**
H-arom.	AA'BB'	7.01	7.00	7.01
-CH(OH)	M	4.02	4.08	4.04
-O-CH_2	D	3.96	3.94	3.95
N-CH_2	M	2.69	2.73	2.49
CH_3-arom.	S	2.28	2.28	2.28
CH_3-CH_2	M	1.49	1.53	1.48
CH_3-CH_2	T	0.92	0.89	0.95
		(12)	**(13)**	
H-arom.*	AA'BB'	7.04	6.98	
H-arom.	AA'BB'	7.01	7.00	
-CH(OH)	M	4.17	4.13	
-O-CH_2	D	4.04	3.99	
N-CH_2	M	3.39	3.42	
CH_3-arom.	S	2.29	2.28	
		(14)	**(15)**	**(11)**
H-arom.	AA'BB'	6.95	6.94	6.94
-CH(OH)	M	3.93	3.98	3.93
-O-CH_2	D	3.94	3.94	3.93
N-CH	Spt			3.07
N-CH_2	M	2.72	2.73	2.58
CH_3-arom.	S	2.28	2.28	2.28
CH_3-aliph.	S	1.11	1.12	1.07*
				1.03*
		(16)	**(17)**	
H-arom.	AA'BB'	6.92	6.94	
-CH(OH)	M	4.09	4.02	
-O-CH_2	D	3.96	3.96	
N-CH_2	M	2.43	2.54†	
N-(CH_3)	S	2.31		
CH_3-arom.	S	2.28	2.28	
-CH_2-CH_2	M		1.58	
		(18)	**(19)**	**(20)**
-CH(OH)	TQ	3.76	3.83	3.65
$(CH_3)_2$-CH	Spt			3.04
N-CH_2-CH	DAB	2.47	2.44	2.52
		2.39	2.42	2.12
CH_3-CH_2	DQ	1.50	1.48	
CH_3-CH(OH)	D	1.14	1.13	1.14
$(CH_3)_2$-CH	DD			1.09
				1.02
CH_3-CH_2	T	0.82	0.89	
		(21)	**(22)**	**(23)**
H-arom.	AA'BB'	6.94	6.94	7.01
-CH(OH)	TQ	4.03	4.05	4.13
-CH_2-CH	DAB	3.23	3.23	3.22*
N-CH_3	S			2.96
CH_3-CH	D	1.26	1.19	1.19
			1.17	

*DD
†6 H
‡D

chemical shifts (δ in parts per million, ppm) and the following notation is used: s, singlet; d, doublet; t, triplet; q, quartet; spt, septet; m, multiplet; dd, doubly doublet; dt, doubly triplet; dq, doubly quartet; tq, triply quartet; AB, dAB, AA'BB' and AA'BB'C spin systems.

Spectroscopical investigations

Mass spectroscopy

The different ways of fragmentation are given in Fig. 6. All reaction products investigated in this work are summarized in Table 6. Investigations were also carried out with some propylene oxide/amine addition products and the experimental data are given in Table 7. The α cleavage to the amino group (Fig. 6, paths a and c) at both possible reaction products (I, II) should lead to stable fragmentations which differ by 30 mass units. Fragmentation b is characterized by the splitting of R^4 (see Fig. 6). The mass of this molecular fragment is the same as that of IIc.

The mass spectroscopic data were obtained from homogeneous reaction products. It is only possible to conclude from these results the formation of the basis molecule I[8], but NMR spectroscopical investigations have to be included.

^{1}H NMR spectroscopy

With 80 MHz ^{1}H NMR spectra the unequivocal structure eludication becomes rather easy by simply analysing the intensities of the proton absorption signals of the two types of N-bonded methylene groups. This will be shown in the case of the monoepoxide/propyl amine mono-addition product. Both possible reaction products (**8, 8a**; Fig. 5) should differ in their integrals by about one proton (see Fig. 7).

The complete attachment of this spectrum can be gathered from Table 4. Here, the region of interest is the one from 2.5 to 3.0 ppm. The integrals of the absorption peaks at 2.6 ppm and 2.8 ppm are exactly equivalent and correspond in both cases to two protons. This suggests that **8** represents the only reaction product[8]. Also, the absorption of a OH bonded, and therefore low field shifted, methylene group has never been observed.

The 300 MHz ^{1}H NMR spectrum allows a more exact analysis of this spin system and leads to the same result. Due to the higher resolution here the absorption at 2.6 ppm can be interpreted as a pseudo sextet of an AB-system. This results from couplings of the NH- combined methylene group with the neighbouring methylene group in the propyl chain. The absorption at 2.8 ppm of the other NH-bonded CH_2-group is accordingly the AB-part of an ABX-system. This system results from couplings of the CH_2-CH(OH)-group. The multiplet at 4 ppm with the intensity of 1 represents the X-part of this spin system corresponding to the single proton at the tert carbon atom in the CH(OH)-grouping (see Fig. 8).

^{13}C NMR spectroscopy

^{13}C NMR spectroscopy leads to the same results[8,9]. Here they will be explained in the case of a monoepoxide/tert butyl amine-monoadduct. Both possible reaction products (**14, 14a**) are given in Fig. 9.

The identification becomes more easy using the *J*-modulated ^{13}C NMR spectroscopy. These spectra were recorded proton broad band decoupled. Therefore every multiplet of ^{13}C-^{1}H couplings breaks down to a

Table 5. Complete ^{13}C NMR spectroscopic data

	$CDCl_3$, TMS;	δ (ppm) [75.5 MHz]		
		(8)	**(9)**	**(10)**
C-arom.				
C-O	S	156.65	156.59	156.86
C-CH_3	S	129.99	130.02	129.82
C-3, C-5	D	129.86	129.86	129.86
C-2, C-6	D	114.39	114.44	114.45
CH_3	Q	20.42	20.42	20.44
C-aliph.				
-O-CH_2	T	70.93	70.34	70.64
-CH(OH)	D	68.13	68.03	66.30
			67.43	
N-CH_2-CH(OH)	T	52.13	58.29	57.39
			57.73	
N-CH_2-CH_2	T	51.68	57.63	56.40
-CH_2-CH_3	T	22.85	20.09	20.33
-CH_2-CH_3	Q	11.67	11.69	11.79
		(12)	**(13)**	
C-arom.				
C-O	S	156.33	156.36	
C-N	S	148.09	148.7	
			147.64	
C-CH_3	S	130.58	130.38	
C-3, C-5*	D	130.00	129.37	
C-3, C-5	D	129.32	129.95	
C-4*	D	118.00	117.62	
			117.01	
C-2, C-6	D	114.43	114.46	
C-2, C-6*	D	113.29	113.68	
			112.37	
CH_3	Q	20.42	20.41	
C-aliph.				
-O-CH_2	T	70.25	69.77	
-CH(OH)	D	68.83	68.55	
			68.11	
N-CH_2	T	46.63	57.66	
			55.36	
		(14)	**(15)**	**(11)**
C-arom.				
C-O	S	156.68	156.53	156.89
C-CH_3	S	130.08	130.10	129.88
C-3, C-5	D	129.86	129.82	129.81
C-2, C-6	D	114.42	114.36	114.42
CH_3	Q	20.43	20.40	20.43
C-aliph.				
-O-CH_2	T	70.81	70.31	70.94
-CH(OH)	D	68.65	70.18	65.65
N-CH_2	D			48.36
N-C(CH_3)	S	50.36	55.93	
N-CH_2	T	44.87	55.62	47.19
-C(CH_3)	Q	29.03	27.12	
-CH-(CH_3)$_2$	Q			22.14
				19.62
		(16)	**(17)**	
C-arom.				
C-O	S	155.93	156.17	
C-CH_3	S	130.61	130.12	
C-3, C-5	D	130.04	129.87	
C-2, C-6	D	114.52	114.47	
CH_3	Q	20.44	20.47	
C-aliph.				
-O-CH_2	T	69.83	70.63	
-CH(OH)	D	64.42	65.43	
N-CH_2-CH	T	60.56	61.27	
N-CH_2-CH	T		54.76	
N-CH_2-CH_2	T		26.13	
N-(CH_3)$_2$	Q	43.95		
		(18)	**(19)**	**(20)**
-CH(OH)	D	65.56	65.23	62.76
			64.13	
N-CH_2-CH	T	57.10	63.77	52.37
			62.69	
N-CH_2-CH_2	T	51.68	57.81	
			57.56	
N-CH	D			48.03
CH_3-CH	Q			22.60
				19.33
CH_3-CH_2	T	23.27	20.29	
			20.27	
CH_3-CH(OH)	Q	20.86	20.65	20.14
			20.43	
CH_3-CH_2	Q	11.70	11.74	
		(21)	**(22)**	**(23)**
C-arom.				
N-C	S	148.20	149.16	150.11
			147.93	
C-3, C-5	D	129.17	129.15	129.09
C-4	D	117.58	117.11	117.08
			116.47	
C-2, C-6	D	113.16	113.78	112.98
			112.06	
C-aliph.				
-CH(OH)	D	66.05	65.79	65.39
			64.90	
N-CH_2	T	51.36	62.32	61.33
			59.91	
N-CH_3	Q			39.27
CH_3-CH(OH)	Q	20.77	20.21	20.30

*N-substituted ring

singlet. The deficit of information concerning the multiplicity of absorption signals which allows distinctions of carbon atoms with respect to their degree of proton substitution will be compensated with the *J*-modulated spin echo experiment. With this technique, quarternary and secondary carbon atoms give positive absorption peaks, tertiary and primary ones negative absorption peaks[10] (see Fig. 10).

N-combined carbon atoms absorb at 45–50 ppm[10]. At 44.86 ppm, the methylene group bonded at the nitrogen atom gives a positive peak. A negative signal of a tert carbon atom as expected in the case of **14a** cannot be absorbed. Absorptions of OH-combined carbon atoms take place at 60–70 ppm[10]. The spectrum shows a negative peak at 68.65 ppm which must be attached to the OH-bonded, tert carbon atom in compound **14**. A positive absorption of a CH_2 (OH)-group as expected for **14a** cannot be detected (see Fig. 11).

Investigations on all other reaction products of epoxides with (6, 7) amines lead to the same results as presented in this example[8] (Table 5).

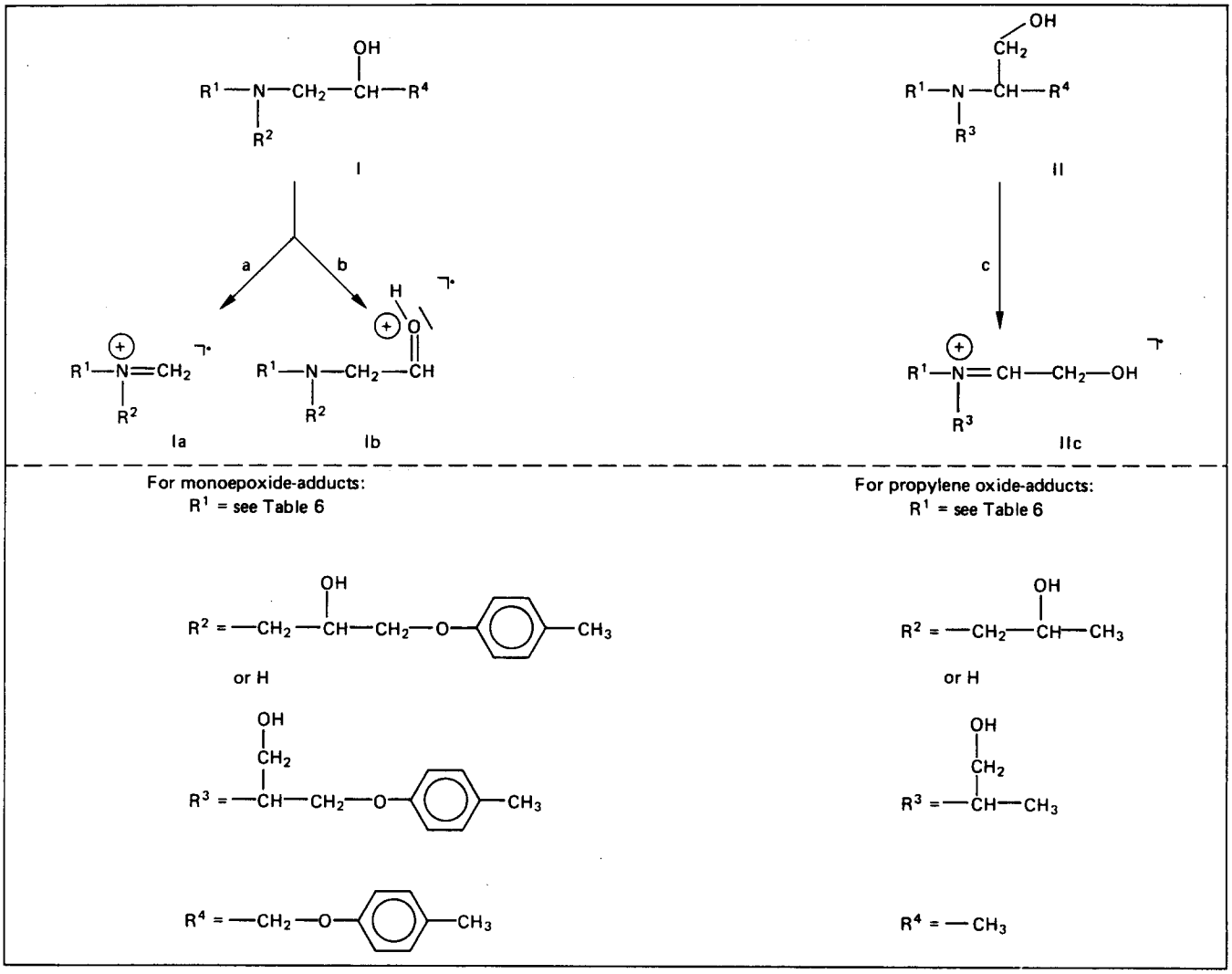

Fig. 6 Methods of fragmentation

Table 6. Substituents of addition products depicted in Fig. 6

I			II		
Compound	R^1	R^2	Compound	R^1	R^2
Monoepoxide/amine-adducts R^4 = -CH_2-O-  -CH_3					
(8)	propyl	H	**(8a)**	propyl	H
(9)	propyl	$C_{10}H_{13}O_2$	**(9a)**	propyl	$C_{10}H_{13}O_2$
(10)	propyl	propyl	**(10a)**	propyl	propyl
(11)	^{i}propyl	^{i}propyl	**(11a)**	^{i}propyl	^{i}propyl
(12)	phenyl	H	**(12a)**	phenyl	H
(13)	phenyl	$C_{10}H_{13}O_2$	**(13a)**	phenyl	$C_{10}H_{13}O_2$
(14)	^{tert}butyl	H	**(14a)**	^{tert}butyl	H
(15)	^{tert}butyl	$C_{10}H_{13}O_2$	**(15a)**	^{tert}butyl	$C_{10}H_{13}O_2$
(16)	methyl	methyl	**(16a)**	methyl	methyl
(17)	piperidyl	piperidyl	**(17a)**	piperidyl	piperidyl
Propylene oxide/amine-adducts R^4 = -CH_3					
(18)	propyl	H	**(18a)**	propyl	H
(19)	propyl	C_3H_7O	**(19a)**	propyl	C_3H_7O
(20)	^{i}propyl	^{i}propyl	**(20a)**	^{i}propyl	C_3H_7O
(21)	phenyl	H	**(21a)**	phenyl	H
(22)	phenyl	C_3H_7O	**(22a)**	phenyl	C_3H_7O
(23)	phenyl	methyl	**(23a)**	phenyl	methyl

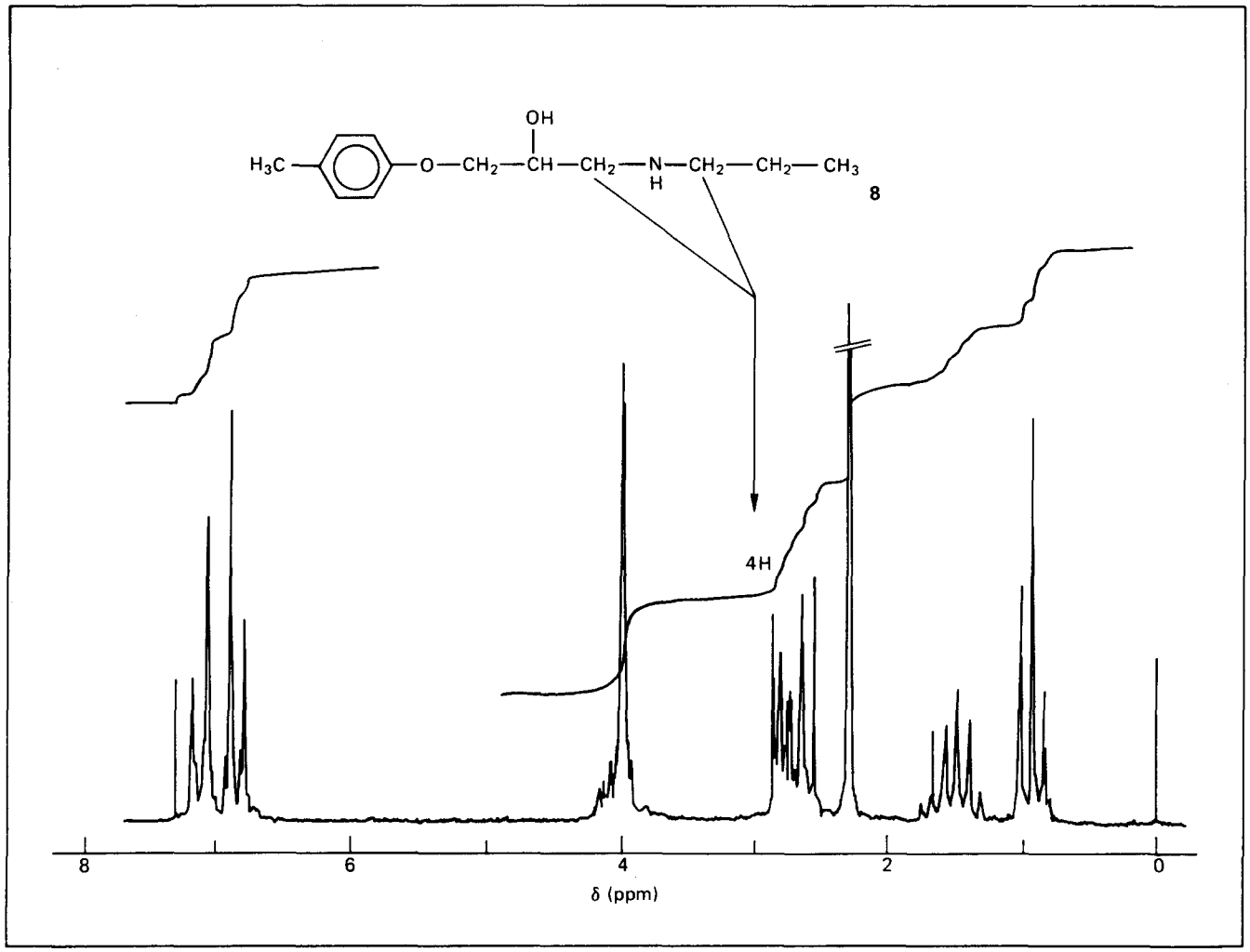

Fig. 7 80 MHz ^{1}H NMR spectrum of **8** ($CDCl_3$, TMS; δ (ppm), 80 MHz)

Table 7. Experimental data

	R^2	R^3	Fragment Ia	Fragment Ib or IIc
Monoepoxide/amine-adducts				
(8, 8a)	H	H	*72* (100)	*102* (3)
(9, 9a)	$C_{10}H_{13}O_2$	$C_{10}H_{13}O_2$	*236* (100)	*266* (2)
(10, 10a)	propyl	propyl	*114* (100)	*144* (3)
(11, 11a)	^{i}propyl	^{i}propyl	*114* (100)	*144* (3)
(12, 12a)	H	H	*106* (100)	*136* (1)
(13, 13a)	$C_{10}H_{13}O_2$	$C_{10}H_{13}O_2$	*270* (100)	*300* (1)
(14, 14a)	H	H	*86* (70)	*116* (4)
(15, 15a)	$C_{10}H_{13}O_2$	$C_{10}H_{13}O_2$	*250* (90)	*280* (2)
(16, 16a)	methyl	methyl	*58* (100)	*88* (2)
(17, 17a)	piperidyl	piperidyl	*98* (100)	*128* (3)
Propylene oxide/amine-adducts				
(18, 18a)	H	H	*72* (100)	*102* (5)
(19, 19a)	C_3H_7O	C_3H_7O	*130* (100)	*160* (3)
(20, 20a)	^{i}propyl	^{i}propyl	*114* (100)	*144* (9)
(21, 21a)	H	H	*106* (100)	*136* (0)
(22, 22a)	C_3H_7O	C_3H_7O	*164* (100)	*194* (1)
(23, 23a)	methyl	methyl	*120* (100)	*150* (4)

Values given in parentheses are relative intensity (%), (70 eV, $m\,z^{-1}$).

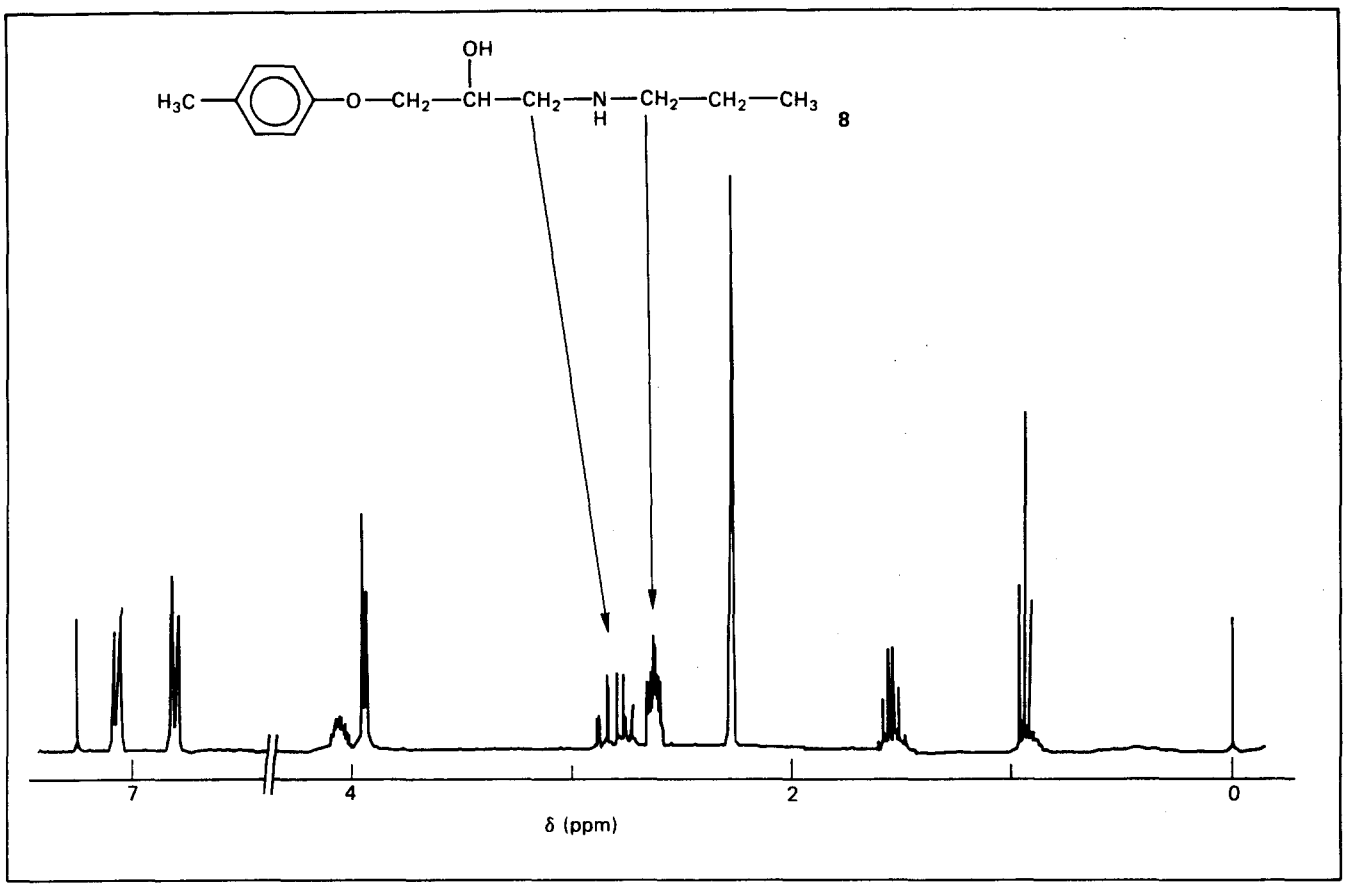

Fig. 8 300 MHz ^{1}H NMR spectrum of **8** ($CDCl_3$, TMS; δ (ppm), 300 MHz)

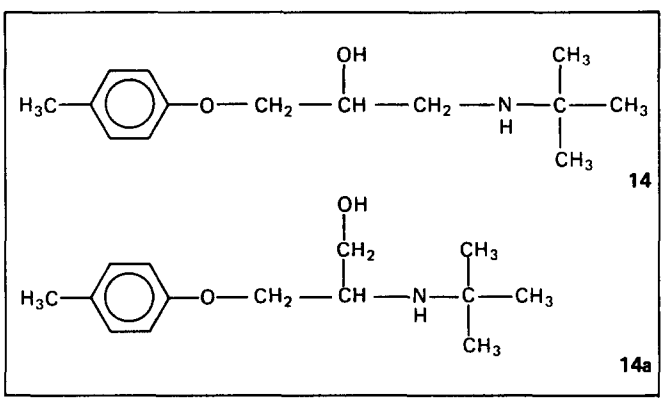

Fig. 9 Formula of **14** and **14a**

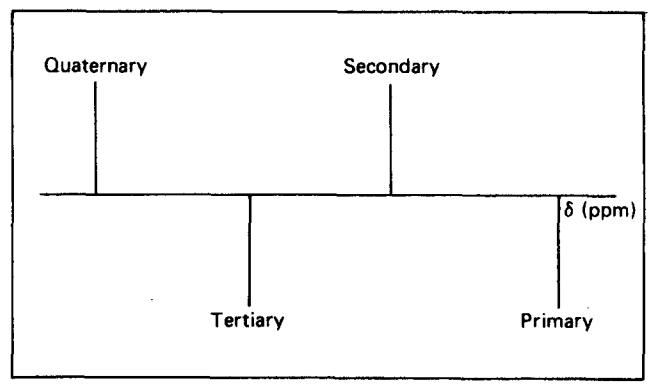

Fig. 10 Scheme of absorption peaks

Conclusions

Compared with bisphenol-A-epoxide (3), a monoepoxide (6, 7), as a monofunctional model compound for epoxide resins, facilitates analytical and preparative seperations of characterizable reaction products. Thus, they can be analysed by mass and NMR spectroscopy. For that reason model reactions are helpful in understanding the formation of epoxy polymers and show an efficient way to characterize them. The investigations suggest that only the terminal carbon atom is attacked by nucleophilic agents. The nucleophilic cure reactions occur *selectively* at this carbon atom in contrast with acidic catalysed epoxy systems. After opening the cyclic three-membered ring with the nitrogen atom of the amine hardener the only reaction products formed in such technical epoxy resins are polymers containing secondary β-aminoalcohol structures. However, any other polymer with a different partial structure will not occur.

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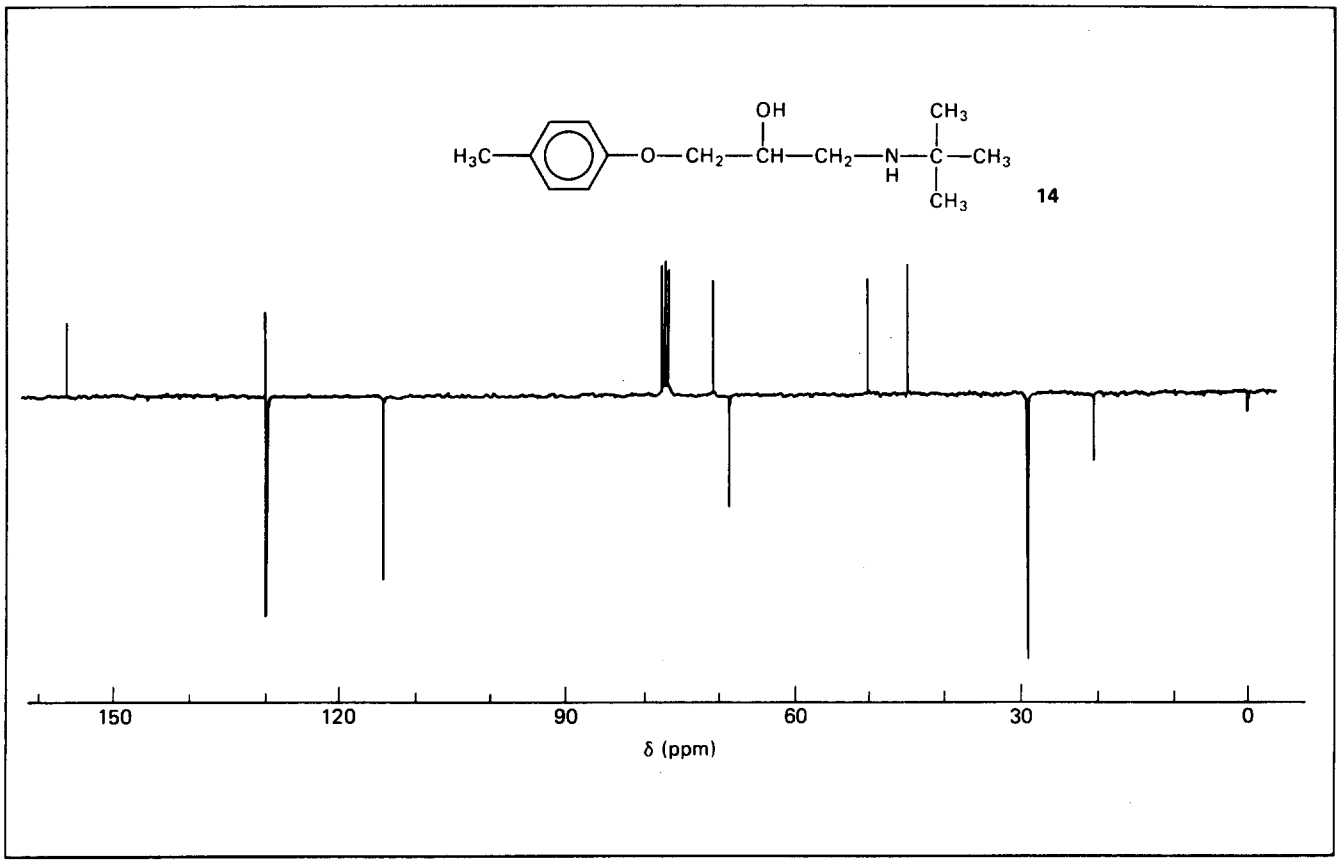

Fig. 11 ^{13}C NMR spectrum of **14** ($CDCl_3$, TMS; δ (ppm), 75.5 MHz)

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