

The microwave reaction of phenyl glycidyl ether with aniline on inorganic supports: a model for the microwave crosslinking of epoxy resins

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The microwave reaction between equivalent amounts of phenyl glycidyl ether and aniline is studied on solid inorganic supports in 'dry media', as a model for the crosslinking reaction of epoxy resins, to determine any chemical peculiarities due to the use of microwave energy. The resulting products are compared with standards given by the conventional heating reaction. The nature of the support is a major parameter. With or without microwaves, clays or silica gel (and especially clays with lamellar structures, such as montmorillonite K10 or Tonsil BW3) provide epoxy conversion extents higher than aluminas, owing to their increased acidic properties. Besides the epoxy-amine addition products, etherification products of the phenyl glycidyl ether are formed by both hydroxyl-epoxy and epoxy-epoxy competitive reactions. When compared to conventional heating, microwaves do not qualitatively change the reaction products, but quantitatively modify their proportions, because both microwaves and the structure of the inorganic supports influence the relative kinetics of the different reaction paths. Copyright © 1996 Elsevier Science Ltd.

(Keywords: aniline; phenyl glycidyl ether; microwave reaction)

INTRODUCTION

During the past 10 years, many papers dealing with the use of microwave energy applied to organic chemical reactions have been published. They have been reviewed by Abramovitch¹ for organic synthesis, by Mijovic and Wijaya² for polymerizations, and by Mingos *et al.*^{3,4} for both topics.

As the energy is directly supplied inside materials, a microwave process offers the advantages of faster and more efficient heating. The 2.45 GHz microwave crosslinking of epoxy resins has already been described by several authors^{5–10}; especially, the effect on the activation of the homopolymerization reaction by the pulse frequency of pulsed microwaves was demonstrated by ¹³C cross-polarization/magic-angle spinning (CP/MAS) n.m.r spectroscopy in solids, showing structural variations in the network of crosslinked resins^{6,7}. Moreover, Singer¹¹ assumed that mechanical property differences observed in microwave-cured epoxy resins might be

attributed to molecular rearrangements induced by the electric field.

Lewis *et al.*^{12,13} discussed the cure kinetics of polyimides from a thermodynamic point of view. Differences between the curves of the microwave solution imidization process and that obtained from conventional heating were shown on Arrhenius plots: the activation energies were found to be 57 and 105 kJ mol⁻¹ for the microwave and the conventional treatment respectively. To explain these deviations, they proposed a model including a non-uniform temperature profile on a molecular scale for the mechanism of the reaction rate enhancement and the decrease in the apparent activation energy.

However, owing to a generally imperfect description of temperature-space-time profiles, all these results did not completely answer the main question: Is there any special effect of the microwave electric field upon the chemical kinetics?

In a series of papers devoted to a mechanistic modelling of the epoxy-amine reaction kinetics^{14,15}, Mijovic *et al.* have shown that the kinetics of the reaction

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between phenyl glycidyl ether and aniline, studied successively in thermal and in 2.45 GHz microwave fields in similar conditions of temperature and pressure, did not significantly differ. But the size of the microwave-cured samples, which can be an important parameter regarding wave-material interactions and heat distribution considerations, was not given. Above all, homopolymerization, which can occur through epoxy-hydroxyl or epoxy-epoxy reactions, although it was described in the model¹⁴, was not taken into account in the experimental results and in the discussion¹⁵.

In fact, experiments with low-molecular-weight model molecules are difficult, owing to the evaporation rate of reagents, which is very much increased by microwaves. The possibility to fix the reagents onto inorganic polar supports provides an opportunity to prevent evaporation until the chemical reaction occurs¹⁶. The coupling of solvent-free techniques with microwave exposure was shown to be of special efficiency in many cases¹⁷⁻²³.

Moreover, many chemistry laboratory researchers are interested in the use of cheap domestic microwave ovens. Thus, and though the best experimental way remains the utilization of monomode microwave appliances in which the distribution of the electric field inside and around samples can be more easily described²⁴, this work was performed in a multimode appliance.

Some preliminary results obtained in this way were presented previously²⁵⁻²⁷. This paper reports the last results dealing with the comparison between microwave exposure and conventional heating, in similar experimental conditions as far as possible, for the reaction of phenyl glycidyl ether with aniline as a model for the epoxy-amine polymerization reaction. Reaction products, including homopolymerization products, were analysed by mass spectrometry and by n.m.r. spectroscopy.

EXPERIMENTAL

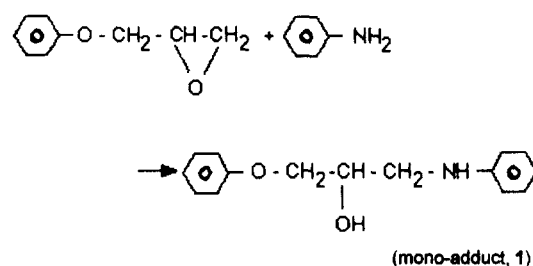
All the experiments were carried out within 3 min in a 2.45 GHz domestic microwave oven (Philips AVM705, nominal microwave power 600 W). The preliminary step was to map the field distribution by means of paper sheets impregnated with a cobalt chloride solution (as described by Villemain²⁷), and then to stabilize this field distribution by using permanent dielectric loads made of alumina-containing dishes, so that the introduction into the oven of a 30 cm³ flask filled with the reagent mixture did not significantly modify this distribution.

Similar experiments were performed under a conventional heating mode: flasks containing the same mixtures were immersed for 3 min into an oil bath, the temperature of the reagent medium being regulated at the value obtained in the corresponding microwave experiment. Useful comparisons were possible between the two energy transfer modes. Nevertheless it must be noted that in both cases the temperature-time and temperature-space profiles were not exactly the same.

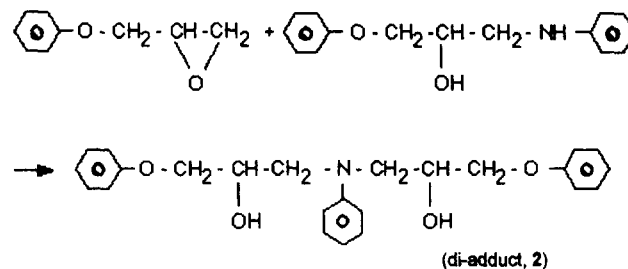
The reagents were a mixture of 10 mmol (1.50 g) of phenyl glycidyl ether (PGE) with 5 mmol (0.47 g) of aniline. They had been previously impregnated onto 1 g of an inorganic support, no solvent being used.

The choice of acidic supports is fundamental as it is widely known that ring opening of epoxides needs electrophilic assistance, which is realized for instance by acidic aluminas, as shown by Posner and Rogers²⁸. Several supports were studied: aluminas, montmorillonite K10 (a lamellar polymeric silicate clay containing sodium, calcium and magnesium cations), Tonsil BW3 (mixed silica and mica in lamellar structures), Florisil (amorphous magnesium silicate) and a kind of powdered silica gel (Silicagel 60). All these supports are either Lewis or Brønsted acids²⁹, so that it was possible to initiate the homopolymerization of PGE, in connection with the interaction of the epoxide oxygen atom with the acid catalyst.

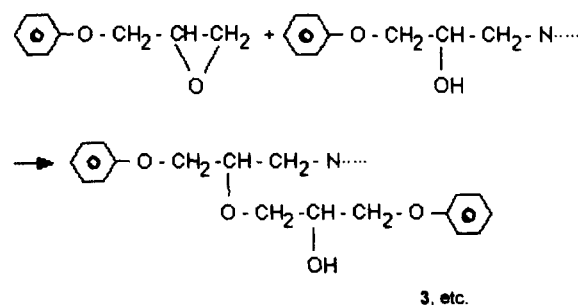
In the absence of catalyst, only two addition reactions would be expected. They are the opening of an epoxide ring by aniline:



and the subsequent opening of another epoxide ring by 1 (N attack):

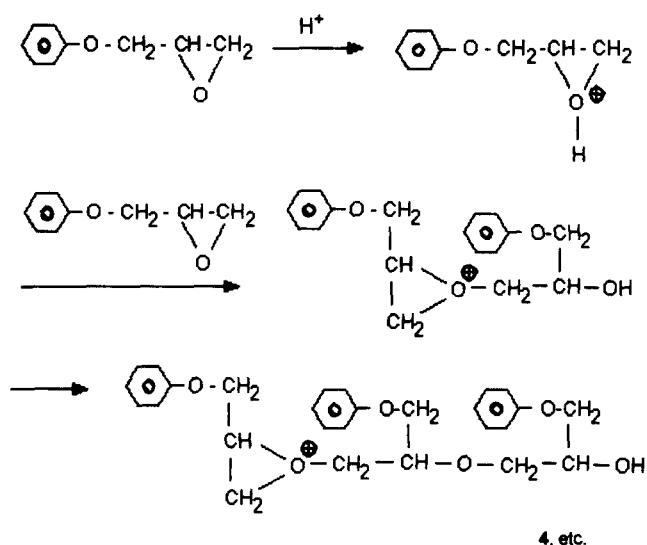


But two etherification side reactions can also occur. The first one is the ring opening of PGE by the hydroxyl functions of adducts 1 and 2, due to their nucleophilic character (epoxy-hydroxyl reaction):



and the second one is the homopolymerization of PGE initiated by the acidic character of the support

(epoxy-epoxy reaction):

*Analysis of the results*

The final mixtures were extracted from supports with ethyl acetate. The solutions were analysed by quantitative gas chromatography (g.c.), determining the remaining amounts of aniline and PGE (and consequently the conversion extent of epoxides), and the quantities of mono- and di-adduct obtained. Letting N_1 and N_2 be the

number of moles of PGE transformed into mono- and di-adduct respectively, the value of the ratio α :

$$\alpha = N_2 / (N_1 + N_2)$$

determines the ratio of di-adduct in the mixture, and thus the reaction rate ratio between the two steps of the addition reaction.

However, a deficit Δ appeared between the number of moles of PGE used and the sum $N_1 + N_2$, i.e. the number of moles of PGE transformed into mono- or di-adduct (Table 1). Moreover, no other compound was detected by g.c., so that the deficit Δ can be attributed to the formation of heavier oligomers due to etherification reactions and remaining attached either to the inorganic supports or the chromatography column, or to both.

Thin-layer chromatography on silica of the ethyl acetate solutions showed six spots. Two of them can be attributed to the remaining PGE and aniline, while the others are related to reaction products, identical whatever the support and the energy transfer mode (microwave or thermal): in every experiment the obtained products were qualitatively the same ones.

The products resulting from several microwave experiments were then separated by qualitative flash chromatography on silica: five fractions were also found, the second of which being separated into two subfractions. In order to determine the chemical structures,

Table 1 Results of microwave experiments. Solid inorganic supports are listed in order of increasing acidity. Initial mixture: PGE, 10 mmol; aniline, 5 mmol; inorganic support, 1 g. Microwave power: 600 W. Experiment duration: 3 min

Support	Final temp. (°C)	Conv. ext. (%)	Remaining (mmol)		Mono-adduct 1 (mmol)	Di-adduct 2 (mmol)	α^a	Δ (mmol)
			PGE	Aniline				
Without	94	3	9.72	3.72	0.00	0.00	0.00	0.28
Florisil	110	89	1.13	0.00	1.26	1.71	0.73	4.18
Basic alumina	121	86	1.42	0.28	2.37	2.27	0.66	1.67
Neutral alumina	108	89	1.11	0.20	1.81	1.57	0.63	3.94
Acidic alumina	112	83	1.69	0.94	2.45	1.60	0.57	2.66
Silicagel 60	132	97	0.30	0.34	2.91	2.09	0.59	2.61
Montmor. K10	130	98	0.21	0.00	2.18	3.31	0.75	0.99
Tonsil BW3	127	97	0.26	0.00	0.77	4.68	0.86	0.00

^a Ratio 2/(1 + 2); see text

Table 2 Results of conventional heating experiments. Solid inorganic supports are listed in order of increasing acidity. Initial mixture: PGE, 10 mmol; aniline, 5 mmol; inorganic support, 1 g. Experiment duration: 3 min. (See exception)

Support	Oil bath temp. (°C)	Conv. ext. (%)	Remaining (mmol)		Mono-adduct 1 (mmol)	Di-adduct 2 (mmol)	α^a	Δ (mmol)
			PGE	Aniline				
Without	94	0	10.00	5.00	0.00	0.00	0.00	0
Without ^b	105	6	4.50	4.55	0.25	0.00	0.37	0.05
Florisil	110	97	0.34	0.00	0.45	1.75	0.89	5.71
Basic alumina	120	83	1.69	0.39	1.87	2.98	0.76	0.48
Neutral alumina	105	81	1.95	0.36	2.02	2.60	0.72	0.83
Acidic alumina	115	80	1.97	0.50	2.40	2.32	0.66	0.99
Silicagel 60	130	86	1.41	0.14	1.59	3.70	0.82	0.00
Montmor. K10	130	100	0.00	0.00	0.82	4.48	0.92	0.22
Tonsil BW3	135	100	0.00	0.00	0.56	4.50	0.94	0.44

^a Ratio 2/(1 + 2); see text

^b Initial mixture: PGE, 5 mmol; aniline, 5 mmol; inorganic support, 1 g. Experiment duration: 8 min

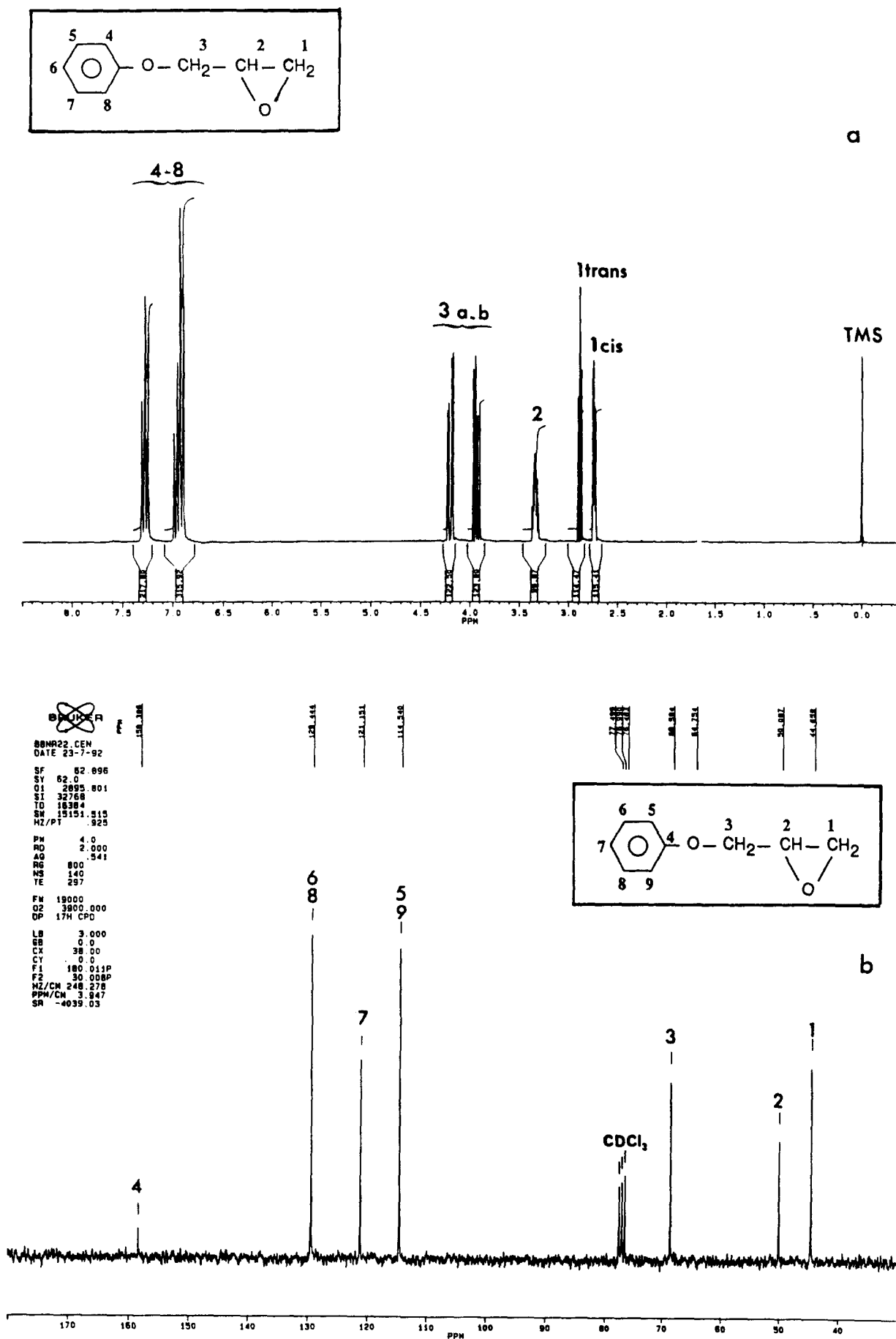


Figure 1 ¹H and ¹³C n.m.r. spectra of the phenyl glycidyl ether (PGE)

every fraction was analysed by mass spectrometry, and by ^1H and ^{13}C n.m.r. spectroscopies.

Analytical data

Quantitative gas chromatography. The separation of aniline, PGE and mono-adduct was performed on a Carlo Erba Vega GC 6000 chromatograph, fitted with a capillary column OV1 (15 m): internal standard, dibutyl phthalate; temperature control, $10^\circ\text{C min}^{-1}$ from 90 to 250°C ; carrier gas, argon at 50 kPa.

The separation of the di-adduct was obtained on a Carlo Erba 4100 chromatograph, fitted with a column SE 30 (1 m) in isothermal conditions (300°C): internal standard, didecyl phthalate; carrier gas, nitrogen at 78.5 kPa.

Qualitative liquid chromatography. This was achieved via flash chromatography on silica; elution was with pentane/ether mixtures of increased polarities.

Mass spectrometry. M.s. was coupled with gas chromatography (Delsi/Nermag).

N.m.r. spectroscopy. ^1H and ^{13}C n.m.r. spectra were recorded either on a Bruker AC200 spectrometer operating at 200 MHz for ^1H and 50 MHz for ^{13}C , or on a Bruker AM250 spectrometer (250 MHz for ^1H ; 62.8 MHz for ^{13}C). All the spectra are referenced to the tetramethylsilane (TMS) resonance used as an internal standard. Measurements were carried out in samples dissolved into deuterated chloroform.

RESULTS

Microwave treatment

In *Table 1* are given the experimental data. In the absence of support, a very low conversion extent was observed, without any production of mono- or di-adduct: only a small amount of oligomers of undetermined structure was obtained (thus confirming the necessity of electrophilic assistance to promote the ring opening of epoxides).

Using aluminas as supports, epoxy conversion extents of about 85% and greater quantities of mono-adduct than of di-adduct were obtained, with important amounts of etherification oligomers, especially on neutral or acidic alumina. In contrast, montmorillonite K10 and Tonsil BW3 exhibited quasi-quantitative conversion extents with high di-adduct formation, but few etherification products; whereas Florisil and Silicagel 60 provided variable conversion extents (quantitative for silica), with high amounts of etherification products.

Comparison with conventional thermal treatment

Without any inorganic supports, no conversion of PGE was obtained, even after an extended heating time of 8 min.

Compared with microwave experiments, conversion extents slightly decreased (80–86%) when using aluminas or Silicagel 60 as supports, but remained 100% on clays. The tendency was of course to obtain more di-adduct, and also less etherification products, except with Tonsil BW3 and especially with Florisil.

Experimental data for conventional heating are summarized in *Table 2*.

Mass spectrometry and n.m.r. analysis

The ^1H and ^{13}C n.m.r. spectra of PGE and of the different liquid flash chromatography fractions are shown in the figures.

Figure 1 shows the ^1H and ^{13}C n.m.r. spectra of PGE, which were used as references for peak assignments.

The first chromatographic fraction, analysed by n.m.r. and mass spectroscopy (molecular weight 243), contains only the mono-adduct **1** ($\text{C}_{15}\text{H}_{17}\text{ON}$). N.m.r. peaks, on both ^1H and ^{13}C spectra, have been assigned according to the proposed formula (*Figure 2*). On the ^1H spectrum, the broad signal (peak number 14) at 2.85 ppm is attributed to both the amino and hydroxyl protons of the molecule, which can be exchanged and engaged in hydrogen bonding.

The second fraction contains a compound whose molecular weight is 393, corresponding to the di-adduct **2** ($\text{C}_{24}\text{H}_{27}\text{O}_4\text{N}$). Its n.m.r. spectra (*Figure 3*) show a splitting of signals attributed to protons 1 and 2 and to carbons 1 and 2 and to the aniline ring. These observations tend to indicate the presence of two different molecules that could have the same molecular weight. But the ^{13}C n.m.r. spectrum recorded at 60°C (*Figure 4b*) presents several changes. Some peaks have drastically decreased (1', 2') and even vanished (10, 13 and the pair 11–15). Similar observations can be made on the 60°C ^1H spectrum (*Figure 4a*): decreasing of the relative intensity of signals 1' with respect to 1. In consequence, this fraction only contains the di-adduct **2**, which can be found at room temperature under two different conformations, probably due to nitrogen inversion, one being stabilized by internal hydrogen bonding.

With regard to the above two fractions, the next two were in small quantities and proceeded from side reactions of little importance.

For the third and fourth fractions, mass spectroscopy measurements provided molecular weights higher than 500.

Figure 5 shows two ^1H spectra. The first one (a) corresponds to the third fraction and the other (b) to a next one. Comparison between spectra on *Figure 4a* and *Figures 5a* and *5b* shows that the latter are more crowded. Nevertheless we are able to distinguish in the central part of the spectra on *Figure 5* (between 3 and 4.5 ppm) three types of protons. On the right-hand part, from 3 to 3.8 ppm are found N-CH_2- protons; from 3.8 to 4.1 ppm the other methylene protons ($-\text{O-CH}_2-$) are found; and the left-hand part is the region of the $-\text{CH}-$ protons. We can also observe that the $-\text{O-CH}_2-$ resonances increase from *Figure 5a* to *Figure 5b* compared to the signals on each side of them. Discrimination between $-\text{CH}-$ signals on *figures 5a* and *5b* at 4.15 (hindered in *Figure 5b*), 4.30 and 4.45 ppm indicates differences between the corresponding ternary carbon atoms. As on *Figure 4a*, signals at 4.45 ppm are attributed to $-\text{CHOH}-$ and the others to $-\text{CHOR}-$, which result from a PGE molecule. In following fractions different reactions can occur: either the second alcoholic proton can be substituted by the same PGE group, or one or the both of them are replaced by PGE oligomers (see below).

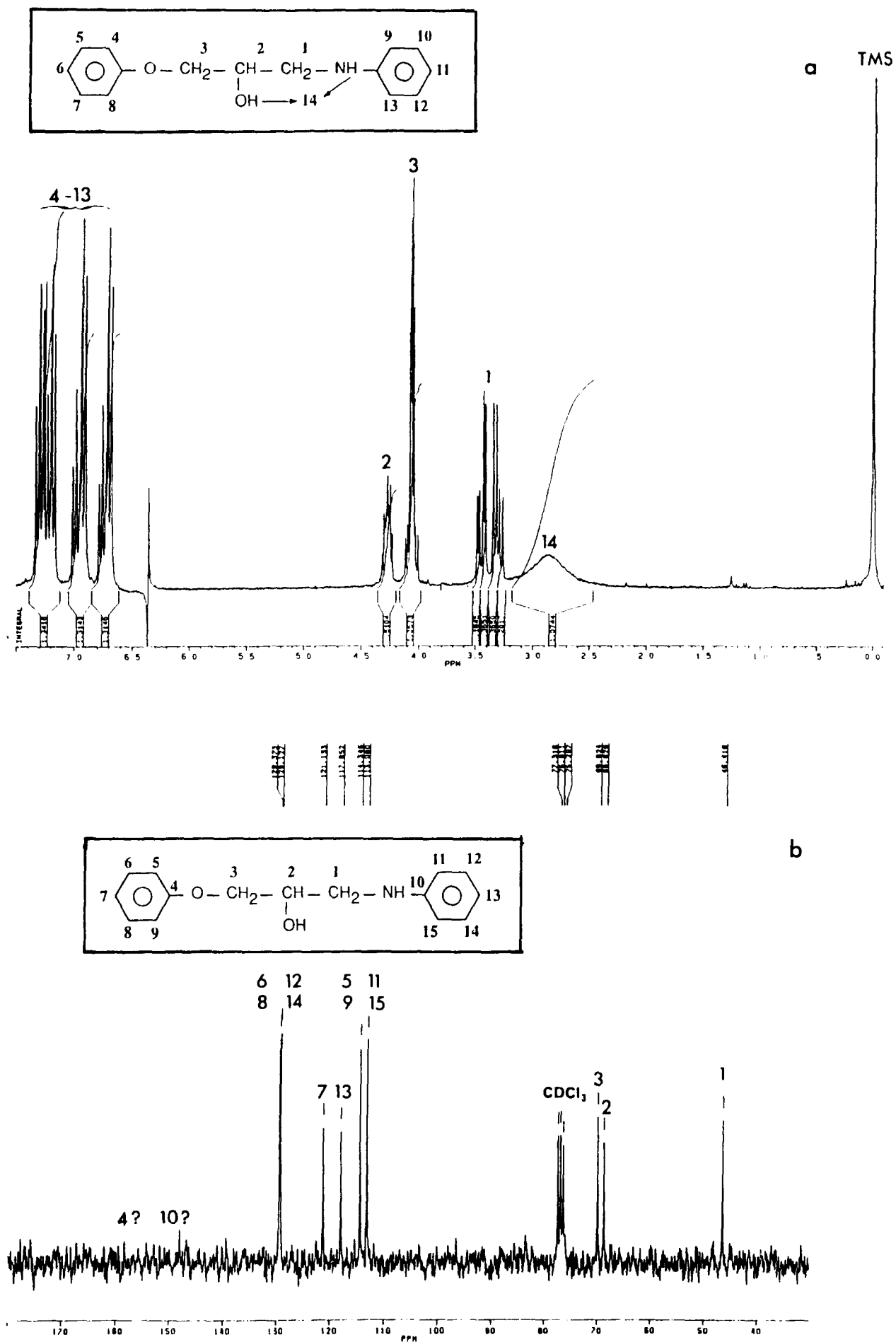


Figure 2 ¹H and ¹³C n.m.r. spectra of the first chromatographic fraction, identified as the PGE-aniline mono-adduct 1 (other comments in text)

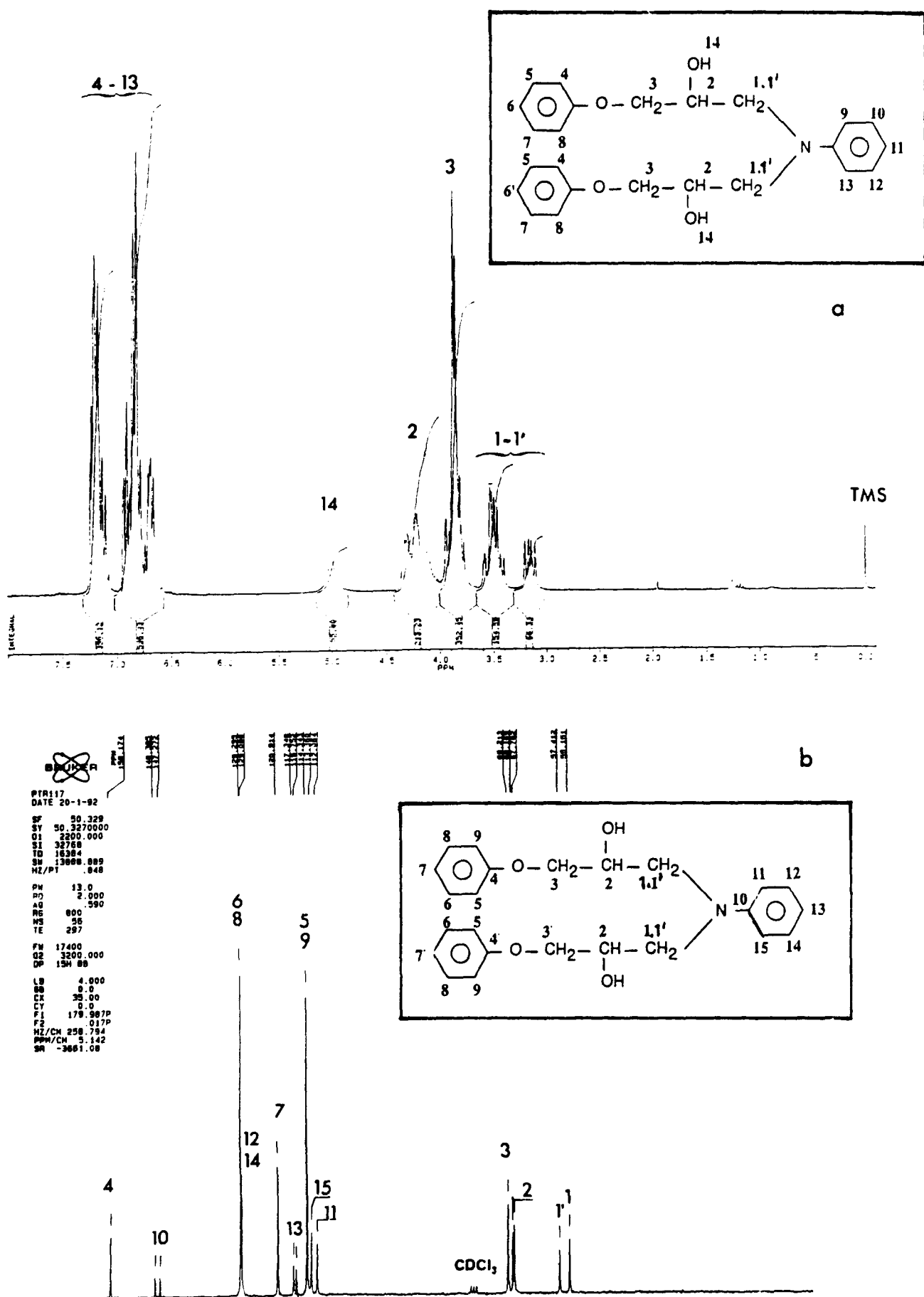


Figure 3 ^1H and ^{13}C n.m.r. spectra of the second chromatographic fraction, identified as the PGE-aniline di-adduct 2 (other comments in text)

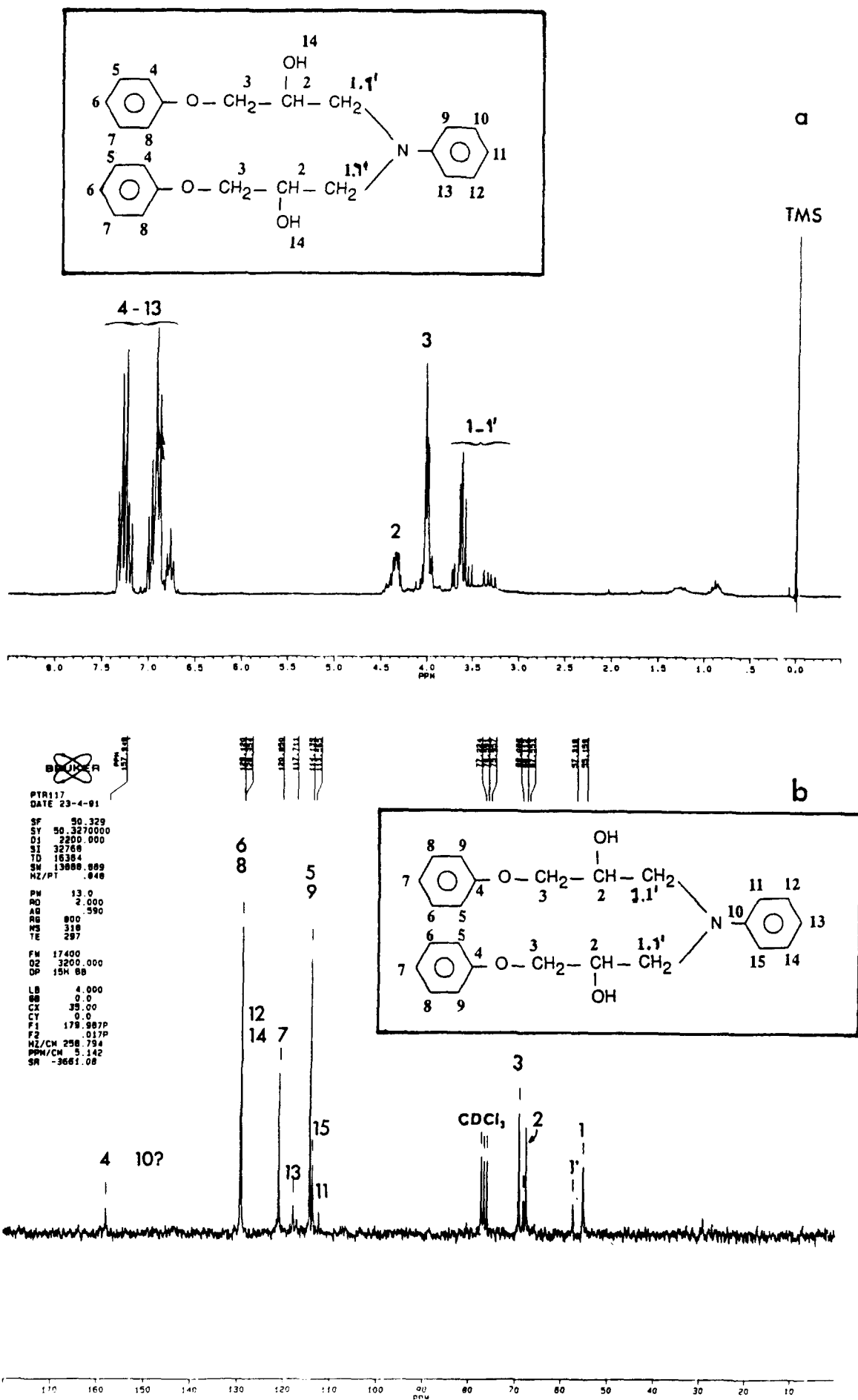


Figure 4 ¹H and ¹³C n.m.r. spectra of the second chromatographic fraction, recorded at 60 C

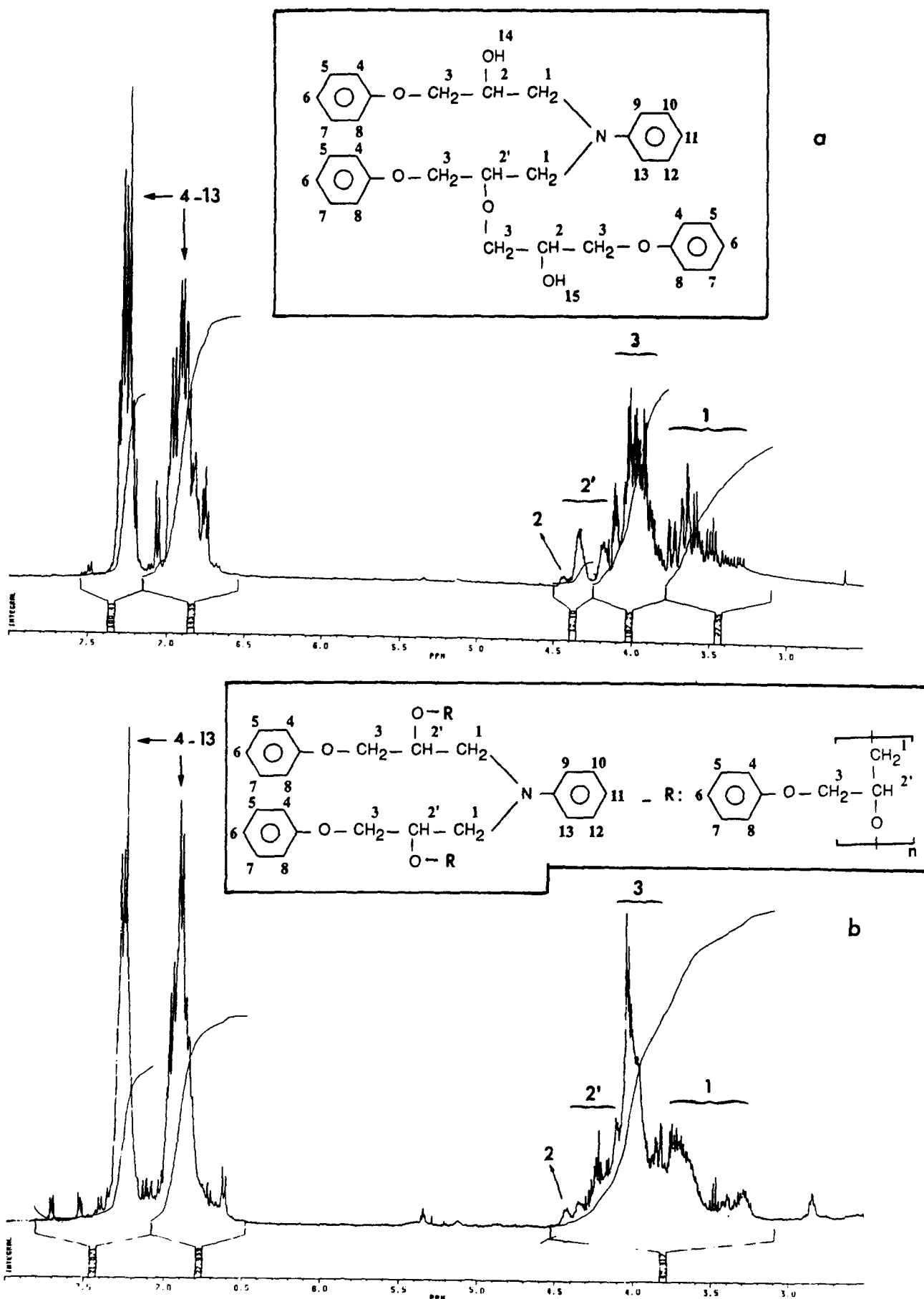


Figure 5 ¹H n.m.r. spectra of the third and fourth chromatographic fractions, identified as PGE-aniline di-adducts with further addition of PGE on the hydroxyl functions; both *a* and *b* might be oligomers of PGE (other comments in text)

^{13}C spectra are not shown because of the complexity of them and the difficulties encountered in carbon assignments.

The molecular weight of the last fraction was also determined to be over 500. The n.m.r. spectra exhibit no signal of ^1H or ^{13}C atoms characteristic of species close to a nitrogen atom (Figure 6). They are spectra of PGE oligomers (4). The weak and broad bands at 3–3.5 ppm in the ^1H spectrum are probably due to hydroxyl ends of short polymer chains. The homopolymerization of PGE occurred, by acidic catalysis due to the solid support, but the relatively low quantity of this compound indicates that this side reaction is not preponderant.

DISCUSSION

Chromatographic separations provided the same number of fractions for all the experiments. For microwave experiments, n.m.r. spectroscopies have shown that every fraction contains only one chemical species, which was successively identified as the mono-adduct 1 and the di-adduct 2 of phenyl glycidyl ether with aniline, and etherification species 3 and 4 obtained either from the mono-adduct or from the di-adduct (3) or by an epoxy-epoxy addition reaction (4), respectively. From a qualitative point of view, there was no difference between microwave and conventional heating modes; noticeably, microwaves did not initiate any new chemical reaction.

From a quantitative point of view, the first important fact is the catalytic effect brought by acidic solid supports. Experiments that were carried out without any support showed very poor conversion extents for PGE, either with or without microwaves, while reagents supported on acidic supports exhibited very large conversion extents (up to 100% in several cases) in very shortened times at the same temperature. This is true as far as temperature was really the same: in fact, temperature estimation is always a problem in microwave experiments. Moreover, heat distribution is always different in microwave and conventional heating: this should be considered as an important parameter in every microwave experiment. A better control of the electric field distribution, and therefore of the temperature distribution, would be afforded by monomode microwave devices.

Considering the results reported in Tables 1 and 2, it must be noted that the higher conversion extents were provided by lamellar supports (montmorillonite K10 and Tonsil BW3, which also are the more acidic) when compared with powdered supports (aluminas, Florisil or Silicagel 60), and by Lewis acid supports (montmorillonite

K10, Tonsil BW3, Florisil, Silicagel 60) when compared with Brønsted acid supports (aluminas). Moreover, the Lewis acids gave higher amounts of di-adduct than did the aluminas, while powdered supports (either aluminas or Lewis acids like Florisil, and except Silicagel 60) provided more etherification reaction products than did the lamellar Lewis acids. It follows that the conversion of epoxides was uniformly accelerated by aluminas providing either epoxy-amine adducts or etherification products, while the epoxy-amine reaction was much more accelerated than the etherification reaction by lamellar Lewis acid supports, the powdered Lewis acid supports being in a median position. An explanation could be given both by the strong catalytic effect of Lewis acids and by a surface state effect, in relation with the granular or lamellar structure of inorganic supports.

This interpretation is reinforced by comparing the conversion extents of epoxides exhibited in Tables 1 and 2. Microwaves generally increased the conversion extent when powder supports are used (except Florisil); with lamellar supports the conversion of epoxides always remains quantitative. Thus we can conclude that the acceleration of kinetics by microwaves was often masked by the catalytic effects of solid supports, and especially of lamellar supports.

Table 3 summarizes the data of Tables 1 and 2 for α and Δ , and gives a comparison between microwave and conventional treatments. The use of microwave energy introduced some differences in the kinetics of the different addition reaction paths. The lower values of α indicate that microwave reactions were always characterized by the formation of lower amounts of di-adduct 2, and consequently the kinetics of the second addition might have been decreased. But greater values of Δ show that microwaves have led to a very increased quantity of etherification products, except for the clays Tonsil BW3 and Florisil. It follows that in fact the etherification reactions leading to oligomers of PGE were accelerated, decreasing the amount of di-adduct.

Thus we can state that microwaves have changed the selectivity between the different chemical reaction paths, decreasing the formation of the di-adduct, and increasing the formation of etherification products obtained by competitive processes, either from the mono-adduct 1 or from the phenyl glycidyl ether itself. But this effect was partly masked by catalytic and thermal effects in supports, which had two consequences:

- (i) The disappearance of a possible microwave acceleration of addition reactions, which were almost uniformly accelerated by the catalytic effect of

Table 3 Comparison between the data exhibited in Table 1 and Table 2. Etherification is obtained by both epoxy-hydroxyl and epoxy epoxy reactions

Support	α		Microwave effect ^a	Δ (mmol)		Microwave effect ^a
	Therm.	Microw.		Therm.	Microw.	
Florisil	0.89	0.73	Di-adduct ↓	5.71	4.18	Etherif. ↓
Basic alumina	0.76	0.66	Di-adduct ↓	0.48	1.67	Etherif. ↑↑
Neutral alumina	0.72	0.63	Di-adduct ↓	0.83	3.94	Etherif. ↑↑
Acidic alumina	0.66	0.57	Di-adduct ↓	0.99	2.66	Etherif. ↑↑
Silicagel 60	0.82	0.59	Di-adduct ↓↓	0.00	2.61	Etherif. ↑↑
Montmor. K10	0.92	0.75	Di-adduct ↓	0.22	0.99	Etherif. ↑↑
Tonsil BW3	0.94	0.86	Di-adduct ↓	0.44	0.00	Etherif. ↓

^a Single arrows, small increase/decrease; double arrows, large increase/decrease

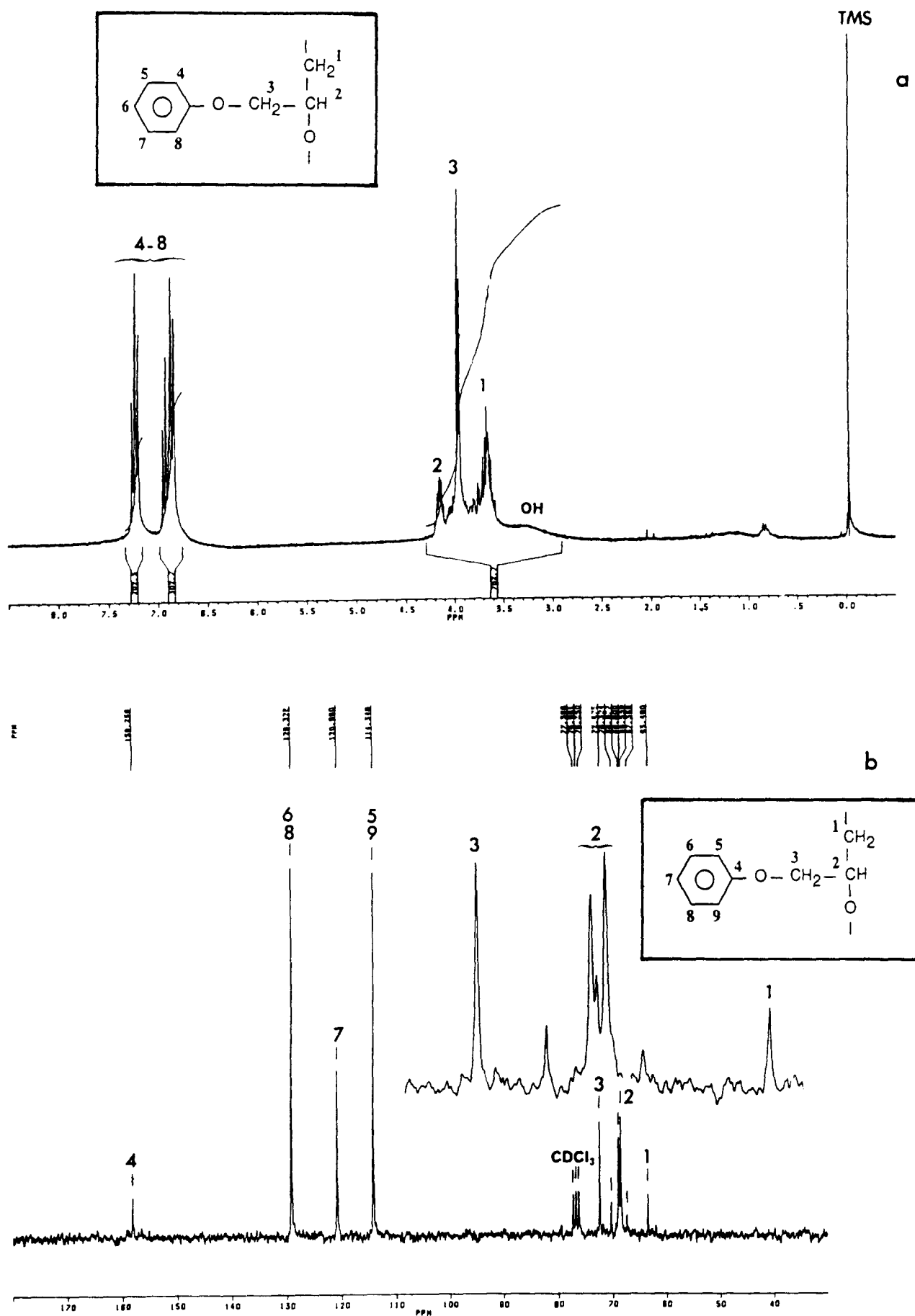


Figure 6 ¹H and ¹³C n.m.r. spectra of the last chromatographic fraction, identified as oligomers of the homopolymerization of PGE (other comments in text)

supports (and especially of lamellar supports), with or without microwaves, and also because of the weak heat conduction in supports, which could have changed the temperature-time profile in samples.

- (ii) Some differences in the kinetics of etherification reactions, including a decrease of the etherification reaction, if using simultaneously microwaves and either Tonsil BW3 or Florisil.

CONCLUSION

The study of the addition reaction between phenyl glycidyl ether and aniline, on inorganic supports and without solvent, as a model of the epoxy-amine cross-linking reaction of epoxy resins, with or without microwaves, has first confirmed the major importance of the chemical nature of the support for the kinetic effects that were observed.

From a qualitative point of view, and compared with conventional heating, microwaves did not initiate any new chemical reactions: the compounds obtained by the two methods of energy transfer were the same.

Nevertheless, from a quantitative point of view, the use of microwave energy was characterized by its influence on the relative kinetics between the possible reaction paths, with consequences on the mono-adduct/di-adduct ratio, and the amplification or the decrease of the etherification reactions, with two concurrent mechanisms: the epoxy-hydroxyl reaction and the homopolymerization of phenyl glycidyl ether, initiated by acidic catalysis due to the inorganic supports.

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