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# The chemistry of novolac resins—V. Reactions of benzoxazine intermediates

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As part of our study on the curing reactions between novolac resins and hexamethylenetetramine (HMTA), a model benzoxazine, 3-(3,5-dimethyl-2-hydroxybenzyl)-6,8-dimethyl-3,4-dihydro-(2H)-1,3-benzoxazine, was heated under carefully controlled conditions, and the structural changes were studied by $^{13}C$ and $^{15}N$ n.m.r. spectroscopy. The benzoxazine structure is relatively stable, and detectable decomposition only occurred about 185°C with the formation of methylene linkages between phenolic rings. Various nitrogen-containing structures, such as amides, amines and imines, together with hydroxybenzyl alcohol, bis(*ortho*-hydroxybenzyl) ether, hydroxybenzaldehyde and *ortho*-hydroxybenzoic acid, are also formed as the side-products of the decomposition. The dominant product after heating the sample to 240°C is 2,2′-methylene-4,4′,6,6′-tetramethyldiphenol. These findings when applied to novolac/HMTA systems provide an explanation for reaction mechanisms/reaction pathways from the benzoxazine intermediates to the final cross-linking network. © 1997 Elsevier Science Ltd.

**(Keywords: novolac resins; hexamethylenetetramine; curing reactions)**

## INTRODUCTION

Hexamethylenetetramine (HMTA) continues to be used as the principal curing reagent for novolac resins to produce cross-linked materials. Previous reports[1–6] have shown that the initial curing intermediates are mainly substituted hydroxybenzylamines (including bis- and tris(hydroxybenzyl)amines) and benzoxazines. Conventional novolac resins contain a high ratio of *ortho*-unsubstituted phenolic positions as reactions sites. When cross-linked with HMTA, benzoxazine and *ortho*-hydroxybenzylamine intermediates are the major intermediates formed at the initial stage. For high *ortho*-linked novolac resins which contain more *para* reactive sites, *para*-hydroxybenzylamines are the dominant first-formed intermediates. Our recent work[6] indicated that not only are the methylene linkages necessary for chain extension and cross-linking formed from these initial intermediates, but various side-products including nitrogen-containing structures in the final cured resins also result. However, the details of the reaction pathways have not been established because the curing of novolac resins with HMTA results in a highly cross-linked polymer network which is insoluble and difficult to study by many conventional analytical techniques. The linewidth of solid-state n.m.r. spectra for these rigid amorphous resins is very broad, and many resonances with similar chemical shifts overlap. Therefore, details of the curing chemistry require further clarification by a solution-state n.m.r. study on carefully designed model systems.

The suitability of 2,4- and 2,6-dimethyl phenols (xylenols), as appropriate model phenol systems for the study of reactions between novolac and HMTA, has long been recognized. The major products from the reactions between 2,4-xylenol and HMTA are 3-(3,5-dimethyl-2-hydroxybenzyl)-6,8-dimethyl-3,4-dihydro-(2H)-1,3-benzoxazine and tris(2-hydroxy-3,5-dimethylbenzyl)amine, while the reactions between 2,6-xylenol and HMTA gives bis- and tris(4-hydroxy-3,5-dimethylbenzyl)amine[5]. We have used these products to study the reactions of benzoxazines, *ortho*-hydroxybenzylamines and *para*-hydroxybenzylamines, respectively, which will be reported in subsequent papers of this series. These model compounds are not expected to form high molecular-weight materials because the remaining two reactive sites on each phenolic ring have been blocked by methyl groups. Therefore, all reaction products are soluble, making it possible to carry out solution-state n.m.r. studies to determine the products formed from thermal decomposition and reactions with phenols. The reaction mechanisms and pathways for the formation of a cross-linked network can be postulated based on these results.

In this paper, we report on the thermal decomposition of 3-(3, 5-dimethyl-2-hydroxybenzyl)-6, 8-dimethyl-3,4-dihydro-(2H)-1,3-benzoxazine using $^{13}C$ and $^{15}N$ n.m.r. spectroscopy. The model compound was made from HMTA labelled with both $^{13}C$ and $^{15}N$, which gives strongly enhanced signals for the nuclei originating from HMTA, thus, the detailed information regarding structural changes during the course of the reactions can be obtained. The possible reaction mechanisms and pathways are discussed. In forthcoming papers we will report on the reactions of benzoxazine intermediates with phenols, and the reactions of hydroxybenzylamine intermediates.

## EXPERIMENTAL

### *Samples*

3-(3,5-dimethyl-2-hydroxybenzyl)-6,8-dimethyl-3,4-dihydro-(2H)-1,3-benzoxazine [structure (**1**) in *Scheme 1*] was synthesized from 2,4-xylenol and HMTA which is 10% C-13 and 99% N-15 enriched, as reported previously[5].

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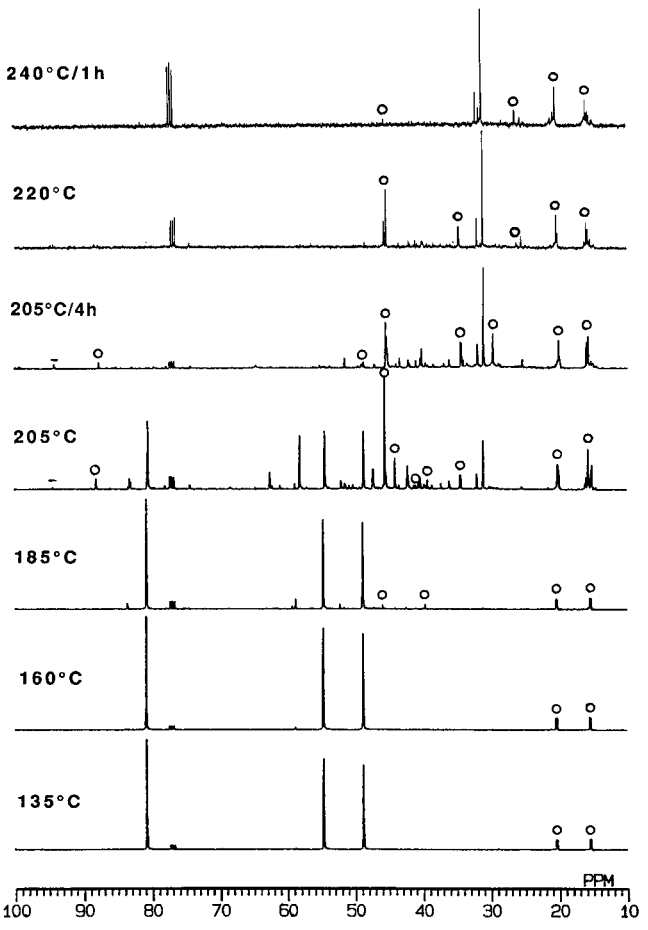



**Figure 1** $^{13}C$ n.m.r. spectra (10–100 ppm range) of the benzoxazine after heating. The (O) peaks appear negative relative to $-CH_2-$ resonances in DEPT spectra

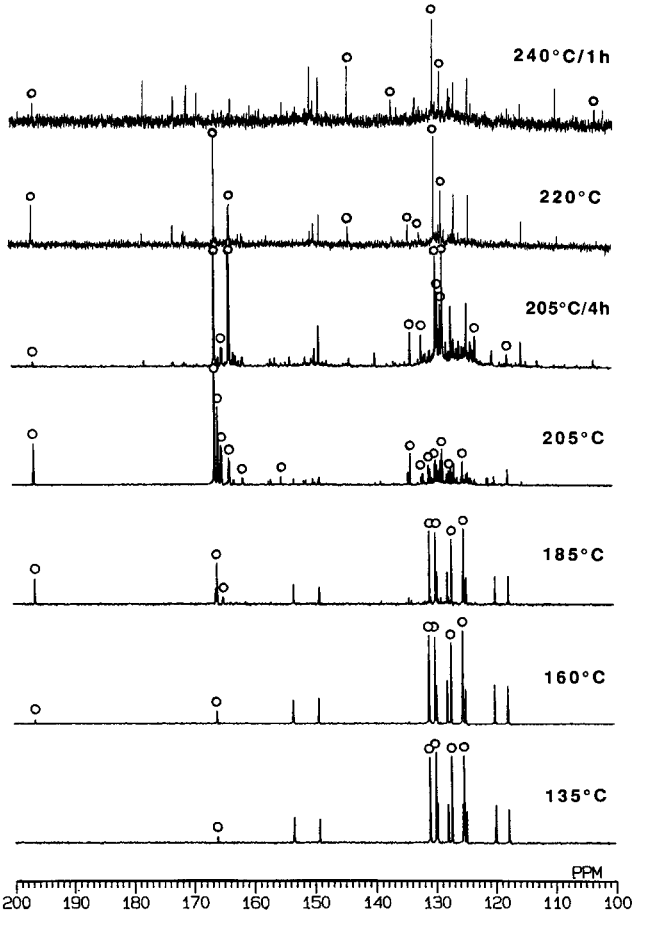



**Figure 2** $^{13}C$ n.m.r. spectra (100–200 ppm range) of the benzoxazine after heating. The (O) peaks appear negative relative to $-CH_2-$ resonances, while the unmarked peaks disappear in DEPT spectra

The benzoxazine (**1**) was heated in a Eurotherm 902 oven at 90°C for 6 h, then the temperature was increased at a rate of 3.7°C $h^{-1}$ until 135°C, thereafter, 12°C $h^{-1}$ until 205°C, 205°C for 4 h, and then 12°C $h^{-1}$ until 240°C and finally heated at 240°C for 1 h. In order to study the structural changes during the heating process, the samples were taken from the oven after heating to 135, 160, 185, 205°C, 205°C for 4 h, 220°C and finally after heating to 240°C for 1 h.

*n.m.r. experiments*

Solution $^{13}C$ and $^{15}N$ n.m.r. spectra were recorded on JEOL JNM-GX400 ($^{13}C$ spectra, $CDCl_3$ (99.8%) as a solvent) and JNM-FX100 n.m.r. ($^{15}N$ spectra, acetone-$d_6$ as a solvent) spectrometers at resonance frequencies of 100 MHz for carbon-13 and 10.1 MHz for nitrogen-15, respectively. $^{13}C$ DEPT spectra were observed by the normal DEPT pulse sequence with $\theta = 135°$. The $\tau = 1/2\ J_{CH}$) was 3.7 ms, and 90° pulse for $^1H$ and $^{13}C$ were 24.6 and 10.0 $\mu$s, respectively. Tetramethylsilane (TMS) was used as an internal chemical shift reference for $^{13}C$ spectra, while HMTA at 44.0 ppm (relative to liquid $NH_3$ at 25°C) in aqueous solution was taken as an external reference for $^{15}N$ spectra.

## RESULTS AND DISCUSSION

The $^{13}C$ n.m.r. spectra of 3-(3,5-dimethyl-2-hydroxybenzyl)-6, 8-dimethyl-3,4-dihydro-(2H)-1,3-benzoxazine (**1**) after heating are shown in *Figures 1 and 2*. In the low chemical shift range (10–100 ppm, *Figure 1*), the peaks marked by open circles are either CH or $CH_3$ and the rest are $CH_2$, while in the high chemical shift range (100–200 ppm, *Figure 2*) the open-circles marked peaks are CH and the rest are quaternary carbons, as detected by the DEPT technique. The three strong $^{13}C$ resonances at 81.8, 54.8 and 49.0 ppm were greatly enriched because they originated from labelled HMTA. The methyl-substituted and *meta*-unsubstituted phenolic carbons are located at 124–131 ppm. The *ortho*-methyl carbons appear at 15.5–15.9 ppm while the *para* methyl carbons are at 20.3–20.5 ppm[5–7]. The intensity of *para* phenolic methyl carbons (20.3–20.5 ppm) does not change during the heating process, and thus can be taken as an internal reference.

The benzoxazine structure is relatively stable, and the signals of (**1**) dominated the $^{13}C$ n.m.r. spectra below 160°C. Then, weak resonances were detected at 165.9 and 57.8 ppm, together with the benzoxazine signals. Significant decomposition (**1**) occurred after heating to 185°C. The relative intensities of benzoxazine decreased with increasing temperature while various new resonances were obtained in a wide range in $^{13}C$ n.m.r. spectra above 185°C (*Figures 1 and 2*). After heating the sample to 205°C for 4 h, no benzoxazine signals could be observed and a large amount of 2,2′-methylene-4,4′,6,6′-tetramethyldiphenol [(**5**) the *ortho–ortho* dimer, $-\underline{C}H_2-$ at 31.5 ppm) was observed. Further heating of the sample to 220°C increased the intensity of the dimer and the intensities of most of the side-products decreases. Heating the sample to

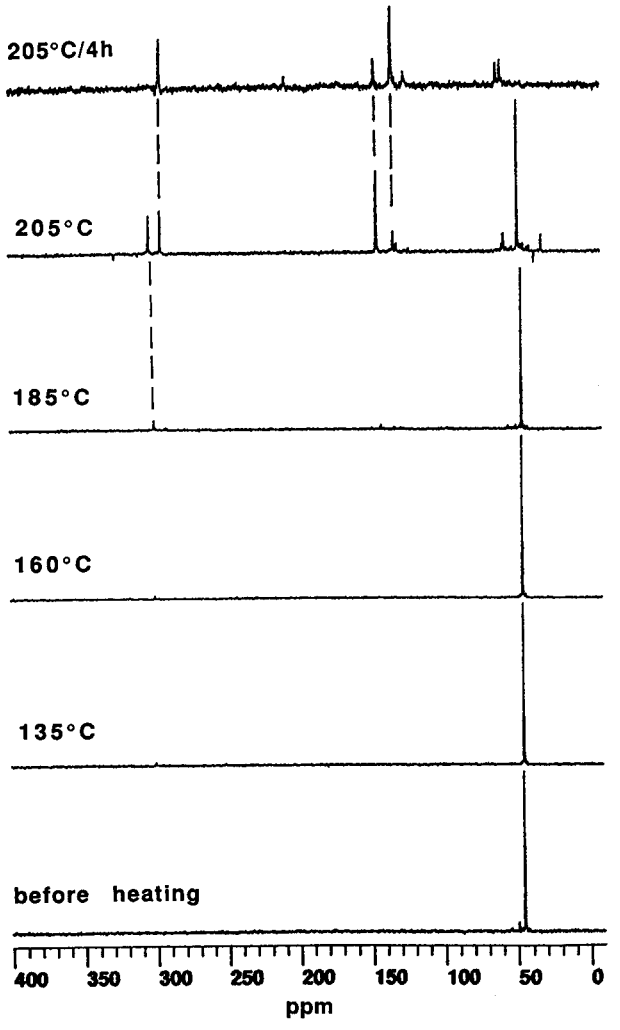
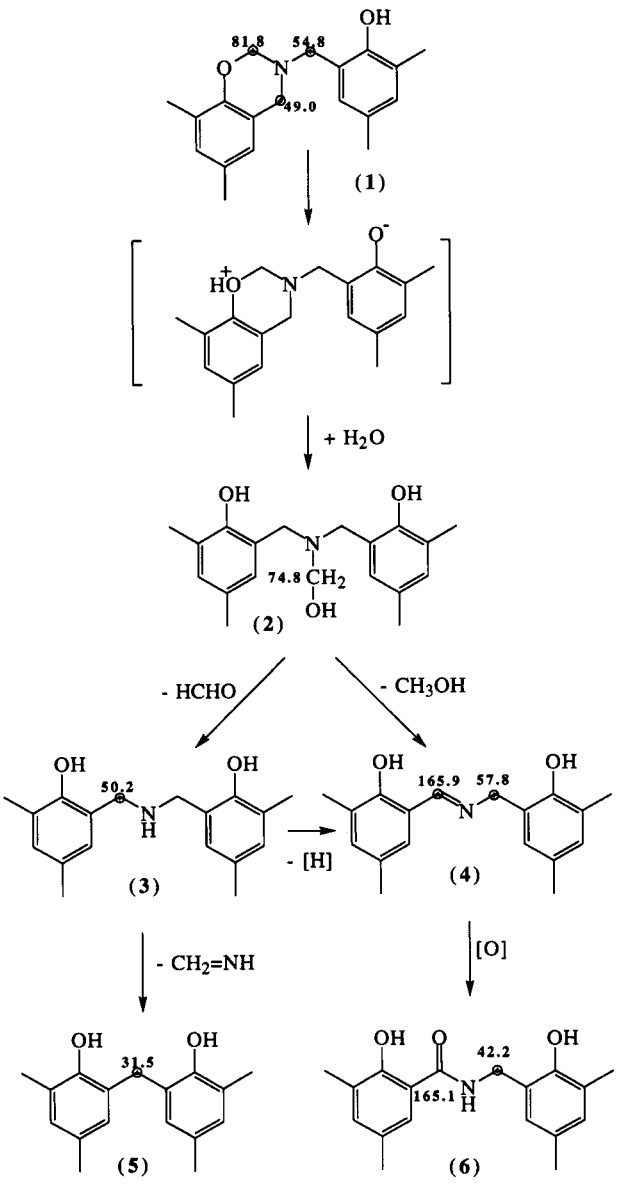



**Figure 3** $^{15}N$ n.m.r. spectra of the benxozazine before and after heating

240°C for 1 h resulted in formation of the *ortho–ortho* dimer as the dominant product while the amount of side-products became very minor. The results provide direct evidence linking the generation of *ortho–ortho* methylene linkages to the decomposition of benzoxazine intermediates.

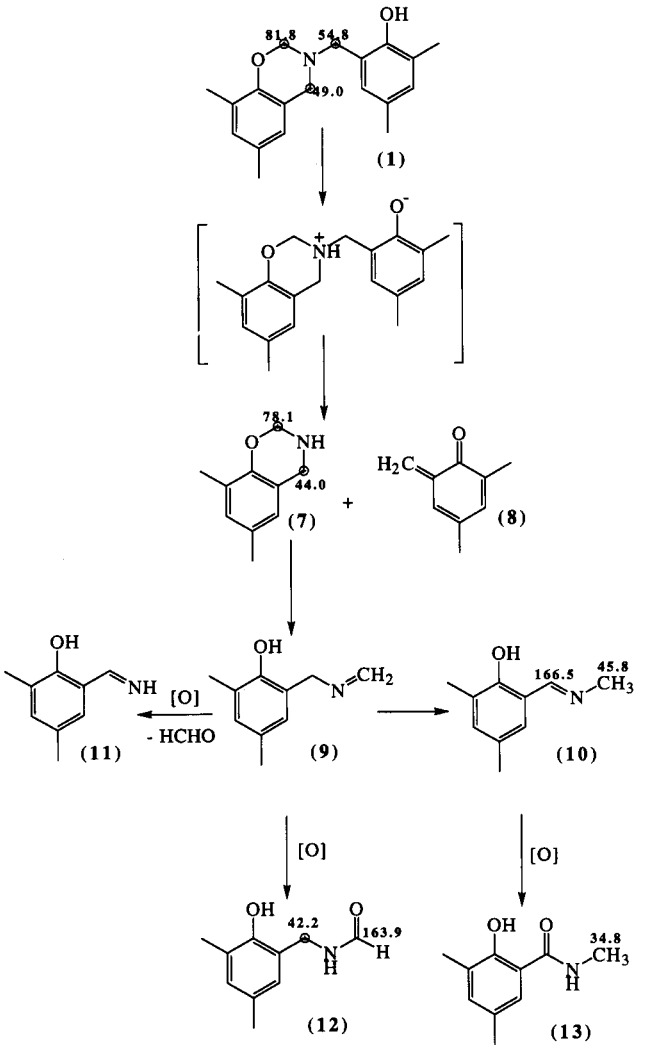
The $^{15}N$ spectra of (**1**) (*Figure 3*) also provide important information regarding structural changes which occurred during the decomposition. The $^{15}N$ chemical shift of (**1**) appeared at 45 ppm before heating, and the resonance disappeared after heating to 205°C for 4 h. Above 160°C, a new peak appeared at 303 ppm, and further heating resulted in various resonances due to imines (303, 295 and 209 ppm), amides (144, 133 and 136 ppm) and amines (61, 58, 40–50 and 31 ppm)[8]. After heating the sample to 205°C for 4 h, the major nitrogen-containing structures were imines and amides.

A detailed analysis of the structural changes during the thermal decomposition/reactions provides information about the reaction mechanism. *Scheme 1* and *Scheme 2* postulate some reaction pathways of the decomposition, together with the key $^{13}C$ chemical shift data of the products. Protonation of the benzoxazine O and/or N probably occurs first, with the proton originating from phenolic hydroxyl groups. The protonation of the benzoxazine N is consistent with a previous report that 92% of hydrogen in $NH_3$ liberated from the curing of substituted phenols with HMTA comes from phenolic hydroxyl groups[9]. Subsequently the benzoxazine structure breaks

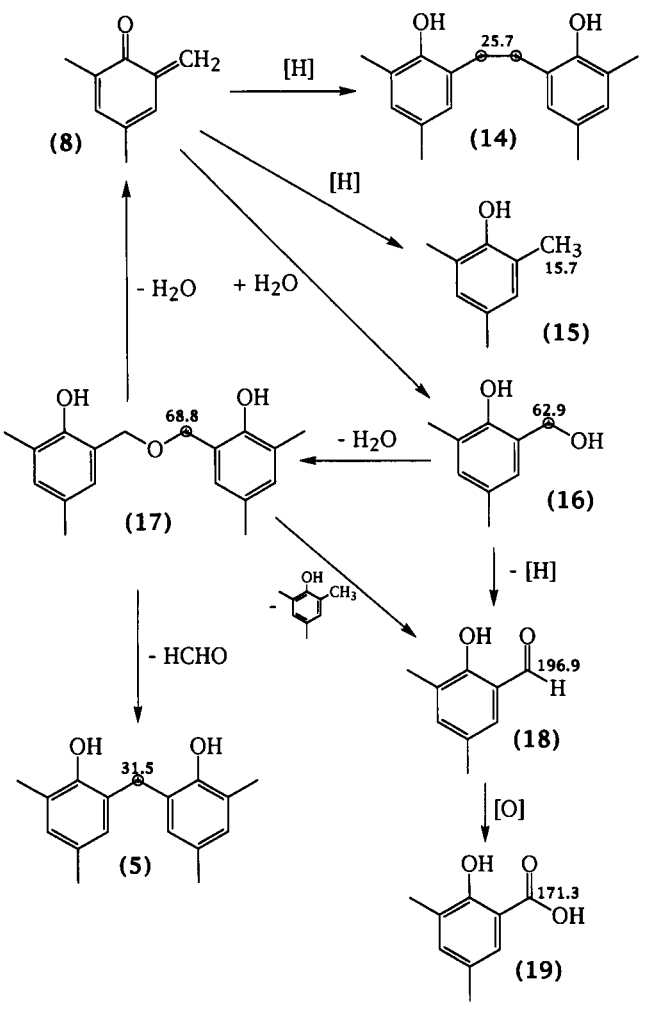



**Scheme 1**

down via either cleavage of the O–C bond or the N–C bond of the six-member ring. The cleavage of the O–C bond could result in the formation of a tertiary amine (**2**) (*Scheme 1*). Resonances at 74.8 or 78.2 ppm are consistent with the >N–$CH_2$OH carbon in (**2**)[10], while the resonances at 50–53 ppm probably correspond to the Ar–$CH_2$–N< carbons. Further heating of the system produces bis(2-hydroxy-3,5-dimethylbenzyl)amine (**3**) (Ar–$CH_2$–NH– carbon at 50.2 ppm), imine (**4**) (the Ar–CH=N– carbon, 165.9 ppm, the =N–$CH_2$–Ar carbon, 57.8 ppm), and the *ortho–ortho* dimer (**5**). Oxidation of imine (**4**) above 205°C results in amide (**6**) (the >C=O and Ar–$CH_2$–NH– carbons at 165.1 and 42.2 ppm[10], and the $^{15}N$ peak at 144 ppm). Meanwhile, the cleavage of the C–N bond (*Scheme 2*) resulted in the formation of 3-methyl-3,4-dihydro-(2H)-6,8-dimethyl-1,3-benzoxazine (**7**) and benzoquinone method (**8**) at first, and then produced imines (**9**) and (**10**). The resonances at 166.5 and 45.8 ppm are consistent with the –CH=N– and >H–$CH_3$ carbons in (**10**)[10] and the $^{15}N$ resonance located at 295 ppm. Oxidation of (**9**) could produce amides (**12**) (the –CHO and the Ar–$CH_2$–NH– at 163.9 and 42.2 ppm[10], and the $^{15}N$ peak at 133 ppm) and (**13**) (the –$CH_3$ peaks at




**Scheme 2**

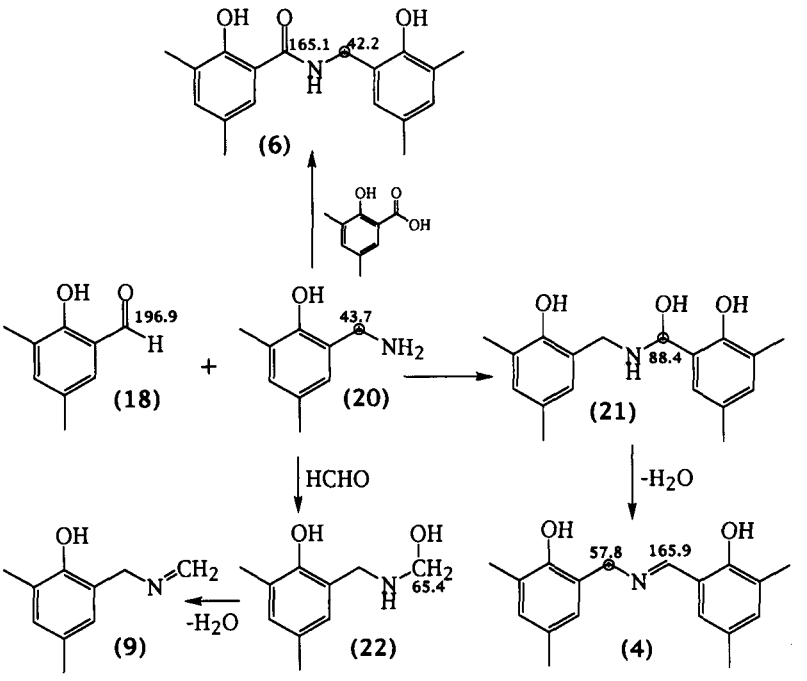



**Scheme 3**

34.8 ppm[10] and the $^{15}N$ resonance at 126 ppm are consistent with the Ar–CO–NH–$CH_3$ structure). No positive $^{13}C$ peak was observed in a range of 100–150 ppm relative to $-CH_2-$ resonance in the $^{13}C$ DEPT spectra which is due to the $-N{=}CH_2$ in imine (**9**). Probably, the imine (**9**) was not stable and decomposed as soon as it was formed at high temperatures. In addition, only imine (**11**) was observed after heating at 205°C for 4 h, and probably (**11**) originated from oxidation following the loss of formaldehyde from imine (**9**) rather than via the reaction between *ortho*-hydroxybenzaldehyde and ammonia.

Benzoquinone methide (**8**) is another major side-product formed from the decomposition of benzoxazine (**1**) (*Scheme 2*) which can undergo various side-reactions. *Scheme 3* summarizes some of the major reactions involving the benzoquinone methide. Radical coupling of two benzoquinone methide units can produce ethylene linkages [(**14**), the $-CH_2-CH_2-$ at 25.7 ppm, above 205°C). Hydrogenation of the benzoquinone methide could produce 2,4,6-trimethylphenol (**15**). Initially the carbon intensities of *ortho* and *para* phenolic $CH_3$ were equal, but after heating to 205°C, the intensity of *ortho*–$CH_3$ (at 15.7 ppm) became higher than that of the *para*–$CH_3$, which was consistent with the formation of tri-methylphenol (**15**). Hydration of the benzoquinone methide produced 2-hydroxy-3,5-dimethylbenzyl alcohol (**16**) (the Ar–$CH_2$–OH at 62.9 ppm)[7] and its condensation gave an ether structure (**17**) (the $CH_2$–O–$CH_2$– carbon at 68.8 ppm)[7]. 2-Hydroxy-3,5-dimethylbenzaldehyde (**18**) (the –CHO at 196.9 ppm[7], above 160°C) and the hydroxybenzoic acid (**19**) (the –COOH at 171.3 ppm, 205°C for 4 h) were formed in the system possibly via dehydrogenation and oxidation at high temperatures. The ether structure (**17**) could also produce the dimer (**5**) by loss of a formaldehyde unit. The $-CH_2-$ peak at 83.5 ppm corresponds to the hydrated formaldehyde (HO–$CH_2$–OH) or formaldehyde dimer[11,12], which can be seen at 185 and 205°C.

Some other possible reaction pathway for forming amides and imines are postulated in *Scheme 4*. The imine (**4**) can also be formed from the reaction between 2-hydroxy-3,5-dimethylbenzaldehyde (**18**) and 2-hydroxy-3.5-dimethylbenzylamine (**20**), followed by dehydration. The peak at 88.4 ppm (a CH as detected by DEPT spectrum) may be due to the >CH– in structure (**21**). 2-Hydroxy-3,5-dimethylbenzylamine (**20**) may also react with formaldehyde to produce imine (**9**) and other imines and amides as shown in *Scheme 2*. The minor resonance at 65.5 ppm at 205°C is consistent with the –HN–$CH_2$–OH carbon in (**22**)[10]. The 2-hydroxy-3,5-dimthylbenzylamine (**20**) may also react with 2-hydroxy-3,5-dimethylbenzoic acid to form amide (**6**). In the $^{15}N$ n.m.r. spectra of (**1**) heated to 205°C, the resonances at 61, 58 and 56 ppm suggest the existence of other forms of amino nitrogen in the system as reported previously[6]. The reactions between formaldehyde and the methylene linkages



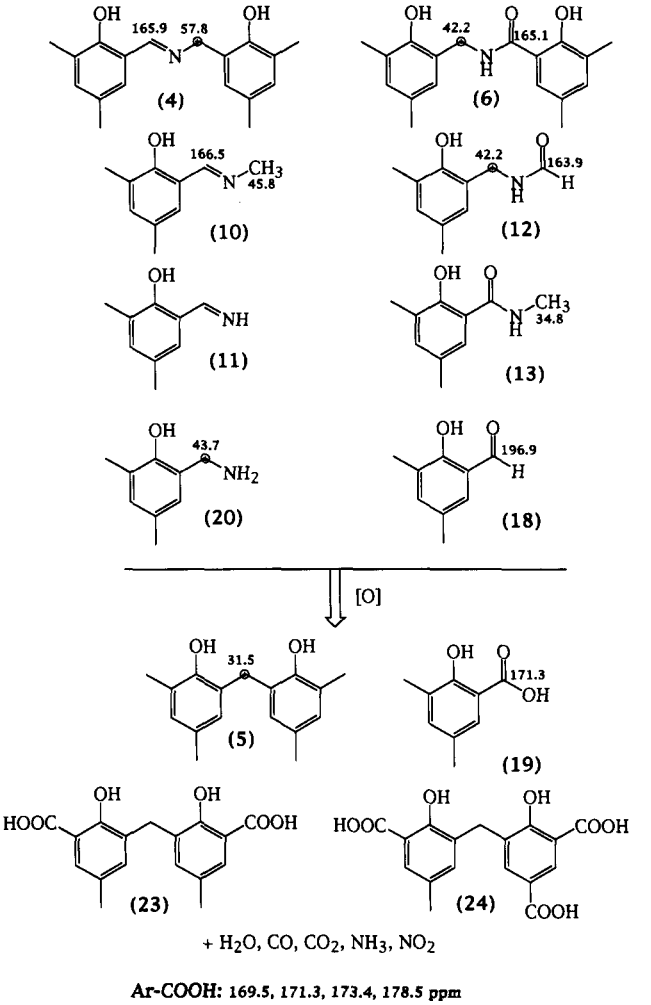

Scheme 4

of the dimer as mentioned in previous reports[11] may also occur at high temperatures, resulting in cross-linking at the methylene linage. The minor resonances around 53–55 and 37–42 ppm are consistent with these products[11].

After heating the sample to 240°C for 1 h, the $^{13}C$ resonances at 166.5, 163.9, 45.8 and 42.2 ppm disappeared, indicating most of amide and imine structures were decomposed and/or oxidized to produce the dimer and other oxidized products, as shown in *Scheme 5*. The new resonances around 169–179 ppm in the $^{13}C$ spectra were observed at 220 and 240°C, and they disappear in the DEPT spectra. Note that the relative intensities of these peaks increase after heating to 240°C for 1 h, and at that time almost no resonances can be observed around 40–43 ppm. Thus, these resonances are not due to the amide C=O, but rather to the COOH carbons which originated from the oxidation of the *ortho* and *para*-methyl groups of the dimer phenolic rings, e.g. (**23**) and (**24**)[7]. The intensity of *ortho*-phenolic $CH_3$ carbon is higher than that of the *para*–$CH_3$ at 205°C, but the two intensities become equal again after heating to 240°C. Since some of the *ortho*–$CH_3$ groups are enriched but no *para*–$CH_3$ is labelled, oxidation of the phenolic methyl group could mainly occur at the *ortho*-phenolic methyl groups. The $-CH_2-$ resonances at 31.9 and 32.3 ppm should be due to the methylene linkages of (**23**) and (**24**), which contain –COOH groups attached to phenolic rings.

## CONCLUSIONS

The $^{13}C$ and $^{15}N$ n.m.r. results provide direct evidence that the thermal decomposition of benzoxazine produces methylene linkages between phenolic rings. In curing novolac resins, this results in chain extension and cross-linking to form a highly cross-linked network. The six-member-ring of the benzoxazine structure is relatively stable up to high temperatures. The decomposition starts with protonation/proton transfer of the phenolic hydrogen to




Scheme 5

the oxygen and/or nitrogen of the benzoxazine, resulting in the cleavage of the six-member-ring benzoxazine structure. Various nitrogen-containing structures, such as amides, amines and imines, can also originate from the side-reactions of the decomposition. These side-products can be also decomposed and/or oxidized at higher temperatures to produce the methylene linkages and other oxidized products. This result is consistent with that observed in the curing study of commercial resins[6].

Therefore, this study has enabled us to postulate detailed pathways for the decomposition of benzoxazine intermediates and to provide a sound basis for observation made of the curing of novolac resins. When conventional novolac resins (containing a high ratio of *ortho*-reactive sites) are cured with a high level of HMTA, benzoxazine intermediates are predominantly produced at the initial stage. Because of the stability of the benzoxazines and other *ortho*-linked nitrogen-containing products, these structures may remain in the resins under curing condition, causing the network built with phenolic rings linked by these nitrogen-containing structures rather than methylene bridges. The properties of the resins, therefore, would be consequently influenced or modified. When a low level of HMTA is used in the curing of novolac resins, some reactive sites still remain after the formation of the first-formed intermediates, and they will further react with these intermediates. The detailed reaction between benzoxazine intermediates and vacant reactive sites of novolac is studied by model systems and reported in the following paper.

ACKNOWLEDGEMENTS

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