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The study of the polyallylation reaction of o-cresol novolac and the regioselectivity of o-allylation vs c-allylation

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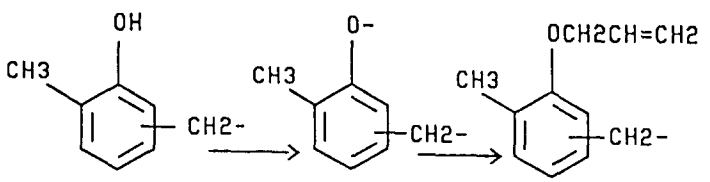
Summary

The polyallylation reaction of c-cresol novolac 1 was achieved in polar aprotic solvents with high phenolic hydroxy conversion(>99%) leading to a unique o-allylation product(>99%). When the reaction was carried out in protic solvent, the c-allylation reaction occurred at about 20-30% along with the o-allylation reaction. Additionally, the phenolic hydroxy conversion was less than 85%. These results showed that the regioselectivity of this reaction was mainly governed by the solvents used. The mechanism of this transformation is briefly discussed in terms of the ambident nature of and solvation effects on the counter ions pair of the phenoxide.

Introduction

The allylation reaction of phenoxide ion 2 is well known, but previous studies were basically limited to phenol or bisphenol A type phenoxide ions in an attempt to improve the performance of existing resins, such as epoxy, unsaturated polyester or other thermosetting reactive oligomers [1-3]. The problems related to this reaction are the low conversion of the phenolic hydroxy to the allyl ether and the side c-allylation reaction , i.e., the allylation took place at the aromatic nuclei. Akabori et al reported that when crown-18-ether-6 was used as catalyst, high conversion and pure o-allylation product of phenol could be obtained[4]. However, their study was limited to monomeric phenol type compounds. Our attempt to use their approach to synthesize pure polyallyl ethers of o-cresol novolac 3 proved unsuccessful. The c-allylation reaction remained at the level of 15% and the crown ether was very difficult to remove from the reaction product. In this work, the synthesis of the neat polyallyl ethers of o-cresol novolac 3 [5] and the factors governing the regioselectivity will be briefly discussed[6-7].



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General methods

Infrared spectra were recorded on a Nicolet 60SX FTIR spectrophotometer. The ^{1}H and ^{13}C NMR spectra were taken in $CDCl_3$ and determined on a JEOL JNM-GX 400 FT NMR spectrometer. Chemical shifts are in parts per million relative to $(CH_3)_4Si$ followed by the multiplicity of the signal in the parenthesis.

The reactants and the solvents were of commercially available quality and were used without further purification. Allyl chloride and o-cresol novolac with softening point 95 deg.c. and equivalent weight at about 118.5 were made by The Dow Chemical Co. All reactions were run under N_2, and all glassware was dried before use.

Synthesis

To a dimethylformamide (1000ml) solution containing 236g(2 eq.)of o-cresol novolac, was added 100g(2.5eq.) of sodium hydroxide at r.t. The mixture was stirred under N_2 for 5hrs at 40 deg. c. The solution turned into dark brown color when the formation of the polyphenoxides 2 was completed. The solution was then cooled down to 30-35deg.c. and 225ml allyl chloride (3eq.) was slowly added within 3-4 hrs. After the addition was completed, the mixture was heated at 35-40 deg. c. for 5 hrs., followed by heating to 45-50 deg. c. for 2 hrs. The mixture was then cooled down and dry ice was added to neutralize excess base. The solvent was rotavaporized off under vaccum at 10mmHg, and 1000ml of 50:50 toluene/MEK was added to the syrupy residue. The solution was washed with water succesively until PH=7. The organic layer was separated and concentrated under vaccum. Polyallyl ethers of o-cresol novolac 3 with light yellow color was obtained in 82% yield without the need of further purification. Some typical analytical data are listed as follows: viscosity= 15000cps at r.t.; Phenolic OH content <0.05% and o-allylation substituents >99%; Total chlorine content < 50ppm.

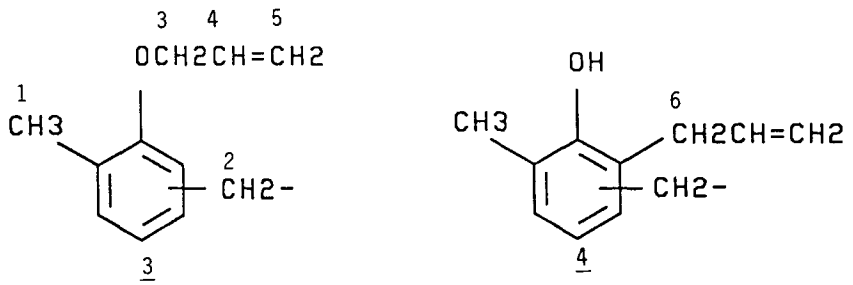
Results and discussion

The desired polyallyl o-cresol novolac ethers 3 were synthesized in two steps via in situ formed polyphenoxide ions 2 under basic condition. Conversion of 2 into 3 was readily accomplished by coupling with allyl chloride at 30-40 deg.c. We observed that in some cases, the c-allylation reaction occurred. Several spectroscopic features for 3 and 4 proved helpful in elucidating the structure. In IR spectra, the broad phenolic hydroxy band for o-cresol novolac 1 occurring between 3400-3600 cm^{-1} disappeared in spectrum 1 which represented the high phenolic hydroxy conversion by using the polar aprotic solvent(DMSO) compared to the spectrum 2 which showed that a certain amount of unreacted phenolic hydroxy remained when methanol was used as the solvent for the allylation. The structures of o-allyl ether in 3 and c-allyl substituent in 4 were readily ascertained from the detailed analyses of the ^{1}H NMR spectra 3 - 4 and Table 1 for ^{13}C NMR spectra.

Table 1. Selected ^{1}H and ^{13}C NMR spectral assignment for polyallyl-o-cresol novolac ethers

Assignment	^{1}H NMR	^{13}C NMR
C-1	2.2-2.3(s)ppm	16ppm
C-2	4.0(br)ppm	30,35,40ppm
C-3	4.0-4.5(d,t)ppm	68,73ppm
C-4	5.7-6.2(m)ppm	111ppm
C-5	5.0-5.4(d,d,t)ppm	116ppm
C-6	3.2-3.4(m,br)ppm	30-40ppm

o-allylation product **c-allylation product**

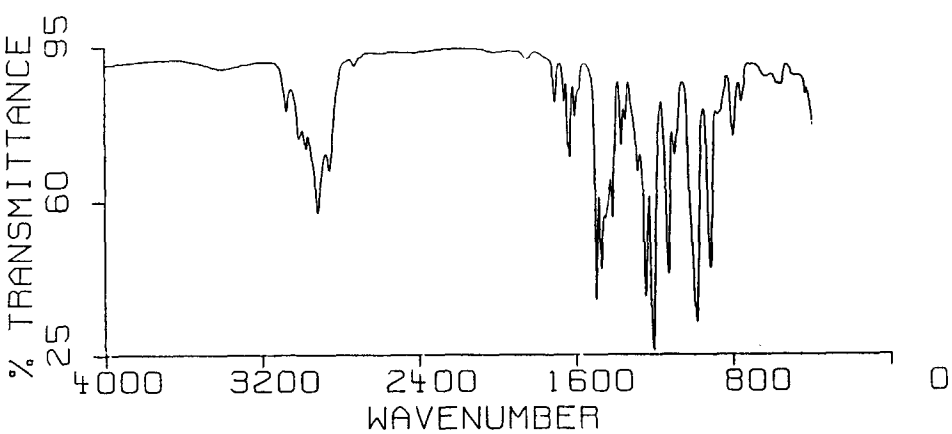


Several features in the NMR spectra agreed with the regioselective formation of the o-allyl ethers and c-allyl o-cresol novolac. The ^{1}H NMR spectrum **3** for polyallyl o-cresol novolac ethers **3** contained a resonance signal at 4.0-4.5ppm for the protons of the allylic methylene hydrogens (C-**3** in table **1**). This signal was slightly overshadowed by the resonance peak of the bridge methylene protons of o-cresol novolac near the 4.0ppm area (C-**2** in table **1**). However, the absorption peaks at 5.0-5.4ppm and 5.7-6.2ppm for the allylic olefinic protons(C-**5** and C-**4**) are unique, and this spectroscopic information is used for diagnoses of the regioselectivity. By comparison of the ^{1}H NMR spectrum **3** (using DMSO as the reaction solvent) with that obtained from the reaction carried out in methanol, a distinguishable proton chemical shift for the c-allylic methylene hydrogens(table **1**, C-**6**) appeared at 3.2-3.4ppm(spectrum **4**). The ratio of the intergration at this region (3.2-3.4ppm) to that for total allylic olefinic terminal protons (5.0-5.4ppm, C-**5** in table **1**) is about 20-30% and this ratio represents the c-allylation percentage in polar solvents. Moreover, the ^{13}C NMR spectra also provided strong support for the regioselectivity difference between the polyallylation reaction in aprotic solvents and protic solvents. In the proton decoupled ^{13}C NMR spectrum, two signals at 68 and 73 ppm were detected. By comparison with the proton decoupled ^{13}C NMR of o-cresol novolac, the resonace peaks at 68 and 73ppm were assigned as o-allylic methylene carbon signals(table **1**, C-**3**). The difference in 5ppm for these two peaks can be attributed to the effect of three different types of bridge methylene carbons in the o-cresol novolac back bone (table **1**, C-**2**, i.e. oo-, op-, pp- substituents, which are located at 30-40ppm area). As the c-allylation reaction took place in the protic solvents, the proton decoupled ^{13}C NMR spectra became much complicated by the appearence of c-allylic methylene carbons(table **1**, C-**6**) in the area of 30-40ppm. As shown in Table **2**, two types of solvents were chosen as test examples for the proposed methods: (1) polar aprotic solvents, such as dimethylformiamide(DMF), dimethylacetamide(DMAC) and dimethylsulfoxide(DMSO); (2) protic solvents, such as methanol, n-propanol and n-butanol. We found that at the same ratio of phenolic hydroxyl group to allyl chloride(1.5eq. allyl chloride/1eq.OH), the polyallylation reaction of o-cresol novolac gave an unique o-allylation product **3**(>99% o-allylation) in polar aprotic solvents with high phenolic hydroxyl group conversion(>99%)[5]. When the reactions were carried out in protic solvents, the c-allylation occurred along with o-allylation, and the phenolic hydroxyl group conversion was low. These results showed that the regioselectivity (o-allylation vs c-allylation) was mainly governed by the solvents used[4].

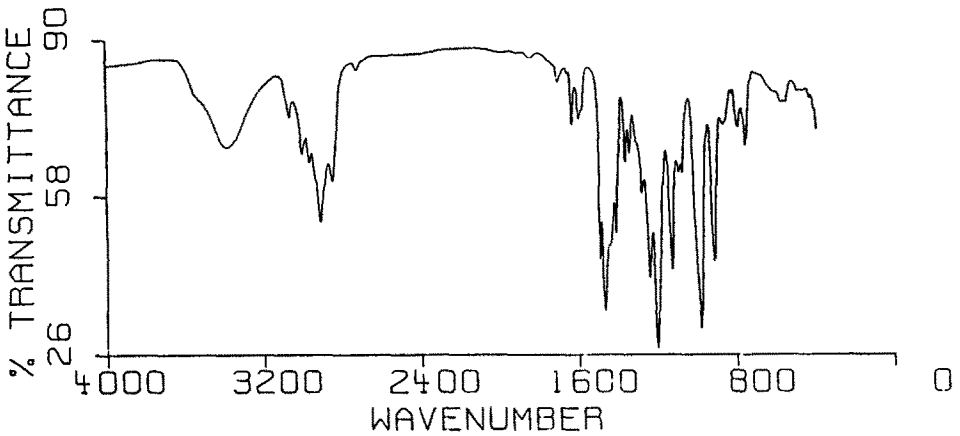
Table 2. Solvent effect on regioselectivity and conversion of polyallylation reactioin of o-cresol novolac

Solvent	Phenolic OH conversion	Regioselectivity
CH_3OH	85%	75%o-allylation 25%c-allylation
CH_3CH_2OH (+crown-18-ether-6)	85%	85%o-allylation 15%c-allylation
n-C_3H_7OH	83%	82%o-allylation 18%c-allylation
n-C_4H_9OH	68%	85%o-allylation 15%c-allylation
DMF	>99%	>99%o-allylation
DMAC	>98%	>99%o-allylation
DMSO	>99%	>99%o-allylation

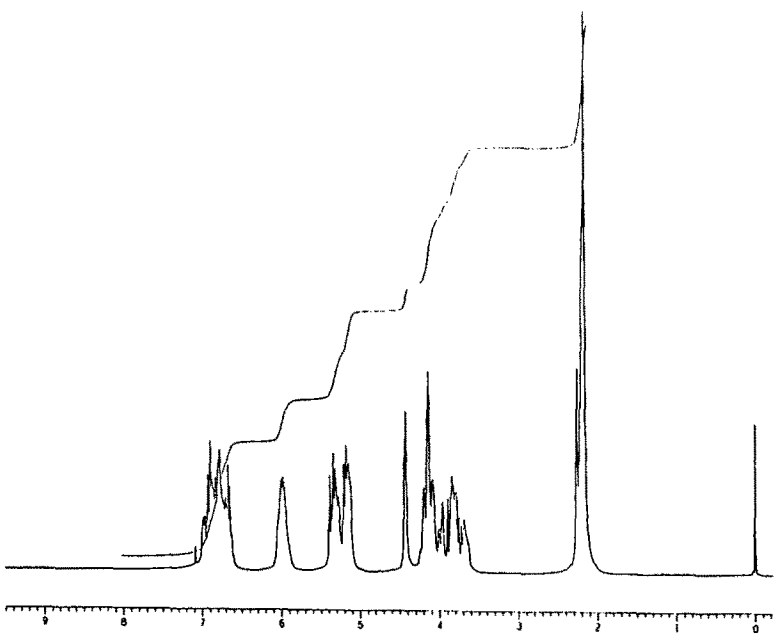
In some examples, crown-18-ether-6 was used in order to improve regioselectivity, however, no substantial change was observed. Besides, the crown ether was difficult to separate from the reaction product.
Phenoxide ion **2** is analogous to enolate ion (**2** vs **5**) and belong to the ambident type nucleophiles[6-7] . The allylation reaction may proceed by o-allylation through **2** ---> **3** or by c-allylation via **5** ----> **4**. In protic solvents, the phenoxide ion was closely paired off with the Na counter ion and solvated by the protic solvent through hydrogen bond, thus, the equilibrium favored **5** which led to the formation of product **4** containing c-allyl substituents. In aprotic solvent, the counter ion Na was solvated , therefore the phenoxide ion **2** was free from entanglement by both the solvent and the counter ion Na, and became very strong nucleophile, leading to o-allylation reaction in >99% specificity. The reaction is also very fast and the reaction course can be followed by the disappearance of the dark brown color of the phenoxide ion **2**.



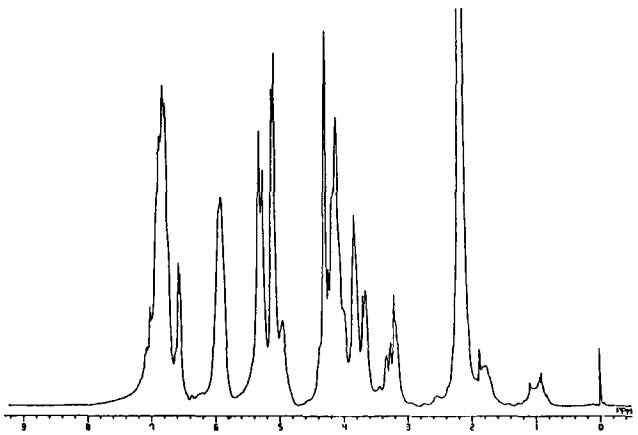
Spectrum **1** IR for poly-allyl ethers of o-cresol novolac (DMSO was used as the solvent for the reaction)



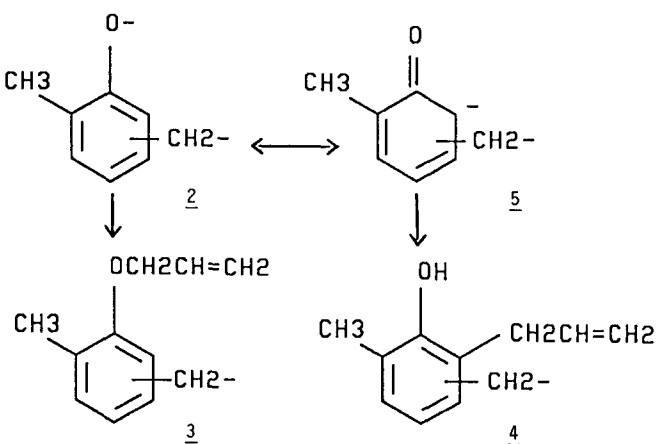
Spectrum 2 IR for poly-allyl ethers of o-cresol novolac
(Methanol was used as the solvent for the reaction)



Spectrum 3 ^{1}NMR for poly-allyl ethers of o-cresol novolac
(DMSO was used as the solvent for the reaction)



Spectrum 4 ^{1}NMR for poly-allyl ethers of o-cresol novolac
(Methanol was used as the solvent for the reaction)



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