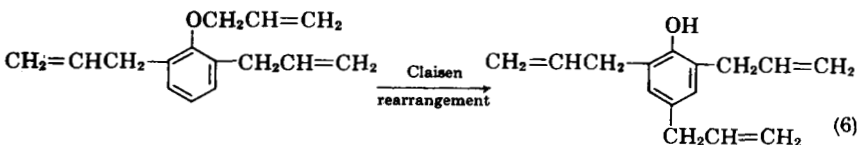
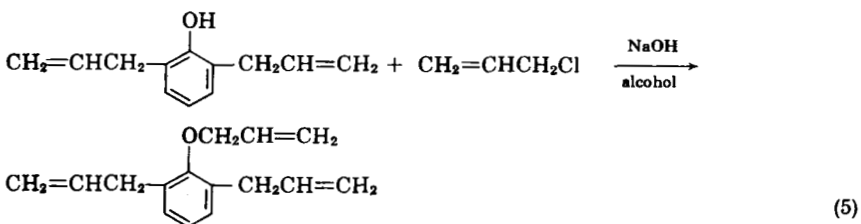
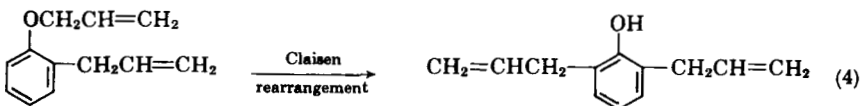
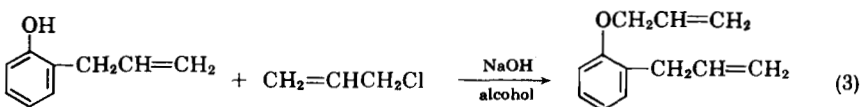
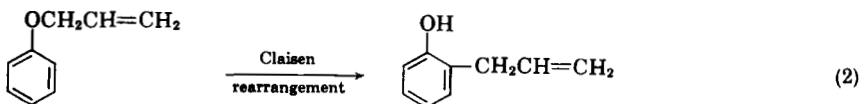
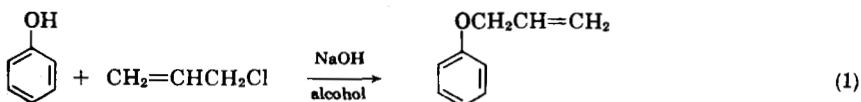
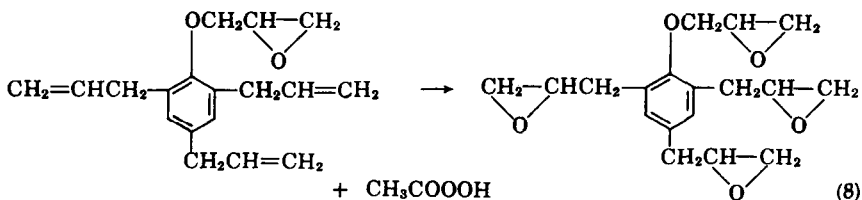
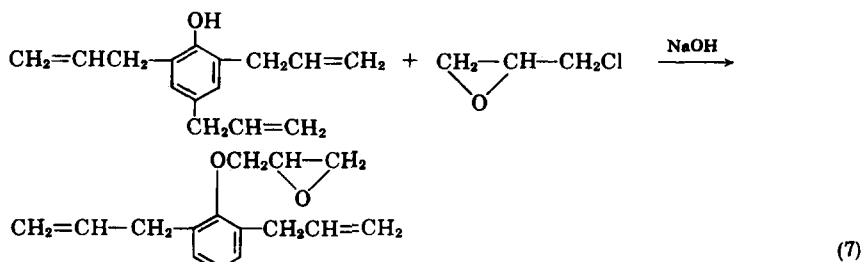


One-Step Polyallylation of Phenols

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It was shown in a previous publication¹ that glycidyl ethers of polyglycidyl phenols when treated with certain amines produce polymers possessing very high heat distortion temperatures. These glycidyl ethers of polyglycidyl phenols were previously prepared by a series of up to eight consecutive reactions. While individually these reactions afforded 70-90% yields, the overall yield was low and the series of reactions was time consuming. This series of reactions may be represented by the equations given below:





To make the end product of this series feasibly commercial it was desirable to cut the number of steps involved in preparing glycidyl ether of polyglycidyl phenol. Claisen² reported that C allylation of phenols is favored over O allylation when the reaction is carried out in nonpolar solvents. It seemed reasonable that polyallylation of phenols could be achieved in nonpolar solvents if an excess of finely divided sodium hydroxide, as well as an excess of allyl chloride, were present and if the water of reaction was azeotropically removed as soon as it was formed. The rapid removal of the water of reaction is necessary to keep O allylation to the minimum, because phenyl ethers do not allylate further unless subjected to a Claisen rearrangement at a higher temperature.

A number of experiments were based on this reasoning and the feasibility of the process was established. It was determined experimentally that the best temperature range for the reaction is 110–120°C. Either powdered sodium hydroxide or azeotropically dried aqueous sodium hydroxide can be used effectively. Potassium hydroxide, lithium hydroxide, nor calcium oxide worked well in the system. After 3 moles of sodium hydroxide and 3 moles of allyl chloride per mole of phenol were used up, no free phenols remained and, therefore, no further allylation could take place.

When but 1 mole of sodium hydroxide was used per mole of phenol the ratio of C allylation to O allylation was slightly better than 2 to 1, and some diallyl phenol was found, as well as unreacted phenol, which is probably due to the competition of phenol and the allyl phenol formed for allylation.

Since polyallylation produces allyl ethers of phenol, monoallyl phenol, diallyl phenol and triallyl phenol, the relatively small amounts of allyl phenyl ether and allyl ether of allyl phenol may be fractionated out, subjected to a Claisen rearrangement, and returned to the allylation reaction. The higher fractions containing predominantly allyl ether of diallyl phenol can be either epoxidized directly or subjected to Claisen rearrangement fol-

lowed by conversion to the glycidyl ether and epoxidation of the latter to the glycidyl ether of triglycidyl phenol. Thus four steps out of eight may be eliminated. The difficulty with direct epoxidation of allyl ethers of polyallyl phenol is that the allyl ethers epoxidize much more slowly than the nuclearily attached allyl groups.

EXPERIMENTAL

Allylation of Phenol, 1:1 Molar Sodium Hydroxide/Phenol

Phenol (188 g.), powdered sodium hydroxide (82 g.), and xylene (750 ml.) were refluxed over a Stark and Dean tube; 37.5 ml. of water collected in the tube. Then 200 ml. of allyl chloride was added at such a rate that temperatures of 110–120° were maintained. The product was cooled, washed with 700 ml. of water, then extracted with 400 ml. of Claisen alkali. The xylene layer was dried over sodium sulfate, filtered, evaporated, and distilled. The distillate weighed 54.5 g. (n_D^{30} 1.5189) and the residue 8 g. Thus the total for neutral product was 62.5 g.

The Claisen alkali extract was acidified with hydrochloric acid, taken up in xylene, washed with water and sodium bicarbonate solution, dried over sodium sulfate, filtered, evaporated, and fractionated through a 1 ft. modified Claisen Vigreux column. Theoretical acid values for allyl phenols are mono 418.6, di 322.4, and tri 262.1.

Fract. no.	Temp., °C.	Press.	Wt., g.	n_D^{30}	Acid no.	Remarks
1	85	6 mm.	26.5	1.5400	469.4	Cont. phenol
2	85–95	6 mm.	16.0	1.5417	426.4	
3	95–100	6 mm.	65.5	1.5417	405.8	
4	100–110	6 mm.	8.0	—	383.5	
5	58–80	40–80 μ	34.0	—	320	Column was re-
Residue			3.0			placed by Claisen
		Total	153.0			head

Polyallylation of Phenol, 3:1 Molar Sodium Hydroxide/Phenol

Phenol (94 g.), powdered sodium hydroxide (41 g.), and xylene (200 ml.) were refluxed and agitated over a Stark and Dean tube (filled with xylene); 18.2 ml. of water collected in the tube. The flask was cooled and a suspension of 82 g. of powdered sodium hydroxide in 100 ml. of xylene was added, followed by 350 ml. of allyl chloride added at a rate to maintain the reflux temperature at 110–120°. The rate of water formation is given below:

Time, hr.	Water, ml.
3	13.5
6 $\frac{1}{4}$	27
13	36.5

Excess allyl chloride was distilled through a 2 ft. column; it weighed 74 g. At 70–90° 2.5 g. came over, at 90–110° nothing came over. Only 1.5 g. distilled between 110 and 130°. The residue was allowed to cool. It was extracted with 600 ml. of water. It took 0.08 mole of hydrochloric acid to neutralize the aqueous extract. The xylene layer was extracted with 200 g. of Claisen alkali. There was no discoloration of the alkaline layer; this indicated lack of free phenols. The upper layer was dried over sodium sulfate, filtered, and evaporated. The product was fractionated through a 2 ft. Dewar Vigreux column topped by a Claisen head.

Fract. no.	Temp., °C.	Press., mm.	Wt., g.	n_D^{20}	I ₂ value
1	50–70	6	23.5	1.5181	275.3
Residue			183.0		369.5
		Total	206.5		

Polyallylation of Phenol, 4:1 Molar Sodium Hydroxide/Phenol

Phenol (94 g.), powdered sodium hydroxide (41 g.), and 400 ml. of xylene were refluxed and agitated over a xylene-filled Stark and Dean tube; 18.2 ml. of water collected in the tube in 45 min. The flask was cooled and a suspension of 123 g. of powdered sodium hydroxide in xylene was added. Allyl chloride (400 ml.) was added to the agitating mixture at a rate such that a reflux temperature of 110–120° was maintained. The rate of water formation is given below:

Time, hr.	Water, ml.
3	16
5	27
6 ¹ / ₂	32
12 ¹ / ₂	36
16 ³ / ₄	37

The product was cooled, washed with 700 ml. of water, dried over sodium sulfate, filtered, and evaporated. Previous studies have shown that at this stage no phenolic substances were present; therefore, no Claisen alkali extraction was used before fractionation. The product was fractionated through a 1 ft. modified Claisen Vigreux column.

Fract. no.	Temp., °C.	Press.	Wt., g.	n_D^{20}	I ₂ value
1	50–70	6 mm.	13	1.5163	203.8
2	70–90	6 mm.	4.5	1.5190	233.1
3	90–110	6 mm.	46.0	1.5206	335.1
4	106	50 μ	131.5	1.5230	379.5
(column substituted by a Claisen head)					
Residue			9.5		
		Total	204.5		

Theoretical iodine values for allylated phenol are mono 190, di 292, tri 356, and tetra 400. Total allylation augmentation was 110.5 g. or $2\frac{3}{4}$ moles of allyl per mole of phenol.

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Synopsis

A process for one-step polyallylation of phenols was developed. Phenol is polyallylated in xylene in the presence of 3 moles of finely divided sodium hydroxide. Three moles of allyl chloride are added at such a rate as to maintain the reflux temperature at 110 to 120°C. Water is continuously azeotropically removed. The product contains allyl ethers of mono-, di-, and triallyl phenol. The bulk of the material is allyl ether of diallyl phenol which can be subjected to Claisen rearrangement followed by glycidyl ether formation and epoxidation of the glycidyl ether of triallyl phenol.

Résumé

On a développé un processus pour la polyallylation de phénols en une étape. Le phénol est polyallylé dans le xylène en présence de 3 moles de soude caustique finement divisée. On ajoute 3 moles de chlorure d'allyle à une telle vitesse que la température de reflux reste entre 110° et 120°C. L'eau est éliminée azéotropiquement sans interruption. Les produits contiennent des éthers allyliques de mono-, di- et triallylphénols. L'éther allylique du diallylphénol forme la plus grande partie, et on peut le soumettre à un réarrangement selon Claisen, suivi de la formation d'éther glycidylique et de l'époxydation de l'éther glycidylique du diallylphénol.

Zusammenfassung

Ein Verfahren zur Einstufen-Polyallylierung von Phenolen wurde entwickelt. Phenol wird in Xylol in Gegenwart von 3 Molen fein verteilten Natriumhydroxyds polyallyliert. Drei Mole Allylchlorid werden mit solcher Geschwindigkeit zugesetzt, dass die Rückflusstemperatur bei 110° bis 120° bleibt. Wasser wird kontinuierlich als Azeotrop entfernt. Das Reaktionsprodukt enthält Allyläther von Mono-, Di-, und Triallylphenol. Die Hauptmenge des Produkts bildet der Allyläther von Diallylphenol, der einer Claisen-Umlagerung mit darauffolgender Glycidylätherbildung und Epoxydierung des Glycidyläthers des Triallylphenols unterworfen werden kann.

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