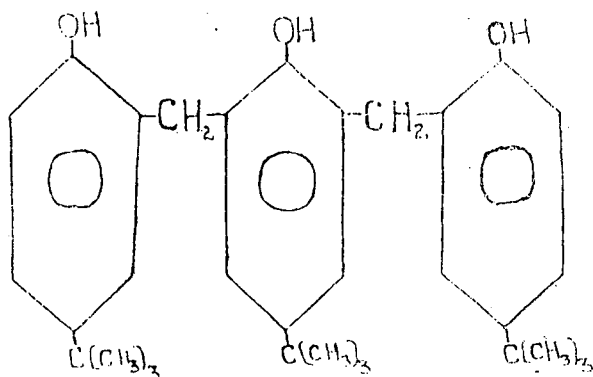


LETTERS TO THE EDITOR

Synthesis of *p*-tertiarybutyl phenolic novolac

Chain molecules in which phenol nuclei are joined by methylene linkage ($-\text{CH}_2-$) constitute the class of compounds called "novolacs". They are generally prepared by the interaction of a phenol with formaldehyde in the presence of an acid catalyst. The acid-catalysed reaction of phenol-formaldehyde has been most thoroughly reviewed by Megson¹ and recently by Solomon.²

In the present work, a novolac resin was synthesised by the interaction of *p*-tertiary butylphenol with formaldehyde at 100°C. using sulphuric acid as catalyst. The resin, after purification, was found to contain three para tertiary butylphenolic nuclei.



The structure of the novolac was established by molecular weight determination and also from the elemental analysis of the acetyl and benzoyl derivatives of the novolac. Infrared spectra of the novolac

and its derivatives are in agreement with the proposed structure of the novolac.

Experimental

The molecular weight was determined by the Rast method³ and compared with the mol. wt. deduced from the hydroxyl number of the novolac. Infrared spectra of the compounds were obtained using Perkin Elmer I. R. spectrophotometer model 337.

Preparation of Para tertiarybutyl phenol^{4,5}

A mixture of distilled tertiarybutyl alcohol (74 g.) and phenol (95 g.) was kept in petroleum ether (200 ml., 40-60°C). Anhydrous aluminium chloride (66.5 g.) was added gradually during one hour so that the temperature was maintained between 25-30°C. The reaction was then continued for 4 hours at that temperature and left overnight. Next day, the mixture was decomposed with ice and hydrochloric acid in the usual manner. The alkylphenol was extracted with ether and the residue was distilled to give para-tertiary butylphenol (65 g.), b.p. 236-238°C. It was recrystallised from petroleum ether as white crystalline solid, m. p. 97-99°C (Lit. 99°C).

Synthesis of p-tertiarybutyl phenolic novolac

A mixture of *p*-tertiary butylphenol (50 g.) in distilled water (20 ml.) and 12N sulphuric acid (1 ml.) was heated to 100°C. Then formaldehyde (13.5 ml; 37-40% BDH) in distilled water (20 ml.) was added

to it in the course of half an hour. The mixture was stirred mechanically for about four hours and kept overnight. The novolac settled down as a viscous mass in the flask and the supernatant liquid was decanted.

The crude novolac obtained (30 g.) was dissolved in methanol and precipitated with water. The oily product was scratched on to the beaker to make it solidify and was filtered. This procedure was repeated and the precipitated novolac (25 g.) was dried *in vacuo*, m. p. 78–80°C (Found: C, 80.65%; H, 9.13%; Mol. wt. (Rast), 462.4; (C₁₂H₁₂O₆ (474) requires: C, 80.83%; H, 9.05%) λ_{\max} 1050, 1360, 1510 cm⁻¹, 2900 and 3050 cm⁻¹.

Benzoylation of the novolac

The novolac (5 g.) was dissolved in pyridine (25 ml.) and was treated with excess benzoylchloride (30 ml.) and heated at 60°C for sometime and left overnight. The mixture was then poured on to crushed ice and the precipitated white solid was collected. It was further recrystallised from dimethylformamide to give the benzoyl derivative as white powder (4 g.), m. p. 149–150°C. (Found: C, 80.87%, H, 6.94%; Mol. wt. 778.5 (Rast); C₁₈H₁₄O₆ (786.96) requires: C, 80.81% and H, 6.99% λ_{\max} : 1100, 1370, 2910, 3040, 1500 cm⁻¹.

Acetylation of the novolac

The novolac (5 g.) in pyridine (25 ml.) with excess acetic anhydride (30 ml.) was

heated on a water bath for about one hour and left overnight. Excess pyridine was neutralised with hydrochloric acid and then poured on to crushed ice. The oily liquid was extracted with ether. After the removal of solvent, the acetyl derivative obtained was distilled *in vacuo* b.p. 241–243°C/2m.m as colourless liquid. (Found: C, 75.80% and H, 8.21% C₁₈H₁₄O₆ requires: C, 75.88% and H, 8.15% λ_{\max} : 1095, 1375, 1520, 2900 and 3400 cm⁻¹.

Acknowledgement

The authors thank the C. S. I. R., New Delhi, for the grant of a Junior Research Fellowship to one of them (B. S. R.) during the period of this investigation.

CLRI, Madras

March 4, 1975

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REFERENCES

1. Megson, J. L., *Phenolic resin chemistry*, Academic press, New York (1958).
2. Solomon, D. H., *Kinetics and mechanisms of polymerisation* Vol. III, Marcel Dekker Inc., New York. (1972)
3. Strachota, J., *Kozarstvi.*, 5, 132, 154 (1955); Rast, K., *Ber.*, 55B, 1051 (1922).
4. Huston, R. C., *J. Am. Chem. Soc.*, 46, 2775 (1924).
5. Samuel Natesan-*J. Am. Chem. Soc.*, 56, 1583 (1934).