Poly-chloronaphthyl

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THE use of ferric chloride as a chlorinating agent and catalyst in organic reactions has been variously reported.[1] Kovacic *et al.*[2] have described the use of ferric chloride with water as a co-catalyst for the

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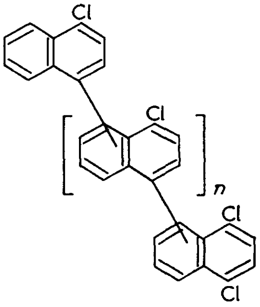
[1] V. Thomas, *Compt. rend.*, 1898, **126**, 1211; **127**, 184; 1899, **128**, 1576. *Bull. Soc. chim. France*, 1899, [3], **21**, 286 P. Kovacic and N. O. Brace, *J. Amer. Chem. Soc.*, 1954, **76**, 5491. "Friedel–Crafts and Related Reactions" Ed. by G. A. Olah, **1**, pp. 279–280, Interscience Publishers, 1963.

[2] P. Kovacic and J. Oziomek, *J. Org. Chem.*, 1964, **29**, 100. P. Kovacic, F. W. Koch, and C. E. Stephan, *J. Polymer Sci., Part A, General Papers*, 1964, **2**, 1193.

polymerisation of benzene. A more recent paper by Kovacic and Koch[3] on the coupling of naphthalene nuclei by Lewis acid catalyst-oxidant, prompted this publication.

As part of a general study of the behaviour of organic compounds in fused salts, the chlorination and polycondensation of aromatic compounds in fused eutectic mixtures containing ferric chloride have been studied. A eutectic mixture of ferric chloride (60%), sodium chloride (26%), and potassium chloride (14%) was found to be a suitable system for studies in the temperature range 150—300°. Under anhydrous conditions naphthalene reacted readily when added to the melt at 200°. Unchanged naphthalene (50%), 1-chloronaphthalene (2·5%), 1,4-dichloronaphthalene, (4·5%), 1,4,6-trichloronaphthalene (1%) (separated by gas–liquid chromatography and identified by infrared spectra, melting points, and analyses) and coloured polymeric solids (40%) were recovered from the melt.



(I)

Fractionation of the polymeric solid afforded a low-molecular-weight, soluble polymer ($\bar{m}$ 1670 corresponding to an average of 10 chloronaphthyl units per chain) and a high-molecular-weight, insoluble fraction with a softening point above 500°. Elemental analyses of the polymers were in agreement with that required for polychloronaphthyl (I). The polymers had excellent thermal stability, being stable in air up to 460° and stable in argon up to 500°. On heating the insoluble polymer to 1000° in argon a weight loss corresponding to dehydrochlorination of structure (I) was observed. The residual material had a graphitic appearance.

In the preparation of *p*-polyphenyl from benzene Kovacic *et al.*[2] postulated a dual role for ferric chloride, as both catalyst and oxidant. Under the anhydrous conditions employed in our fused-salt experiments the reaction sequence for the formation of poly-chloronaphthyl is probably (*a*) chlorination, (*b*) dehydrochlorination and polycondensation. Ferric chloride appears to act as both a chlorinating agent and a Friedel–Crafts type catalyst. In view of the observed presence of 1,4,6-trichloronaphthalene in the reaction media, the possibility of the formation of crosslinked polymers cannot be excluded.

Other aromatic compounds including benzene, anthracene, and dibenzofuran also react with ferric chloride to yield chlorinated monomers and polymers. The reaction of aromatic systems with anhydrous ferric chloride in refluxing carbon tetrachloride also affords chlorinated polymers. These results will be published in detail at a later date.

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[3] P. Kovacic and F. W. Koch, Polymer Preprints 6, 64, 149th Meeting, ACS, April, 1965.