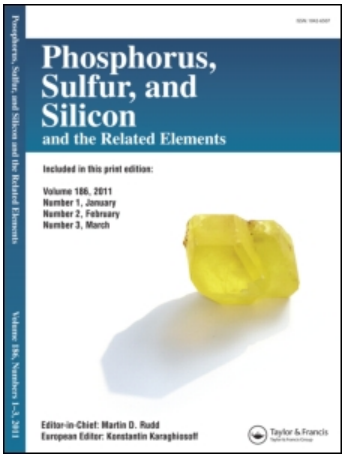

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SULPHENE INTERMEDIATES IN THE SYNTHESIS OF POLY(P-BENZENE-SULPHONAMIDES) AND POLY(P-BENZENE SULPHONATES)

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SULPHENE INTERMEDIATES IN THE SYNTHESIS OF POLY(p-BENZENE-SULPHONAMIDES) AND POLY(p-BENZENE SULPHONATES)

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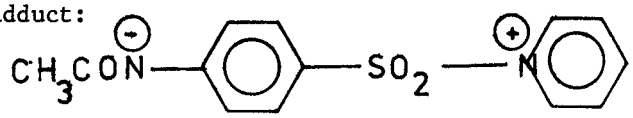
Poly(p-benzamide)(I) and Poly(p-hydroxybenzoate)(II) have recently emerged commercially as high performance materials with unique properties, the first as the basis of high strength and high modulus fibres and the latter as an engineering plastic with excellent high temperature characteristics. In the course of work directed to the synthesis of the structurally related poly-(p-benzenesulphonamide)(III) and poly(p-benzenesulphonate)(IV) and their substituted derivatives we have looked for evidence for the intermediacy of the sulphenes (V) and (VI) respectively:

In the synthesis of (I), the key intermediates are the N-sulphinyl derivative of 4-aminobenzoyl chloride and the hydrochloride of 4-aminobenzoyl chloride. Starting with sulphanilic acid, we have prepared the corresponding N-sulphinylaniline-4 sulphochloride(VII) and aniline hydrochloride-4-sulphochloride(VIII). By controlled hydrolysis of (VII), we have also succeeded in isolating aniline-4-sulphochloride(IX) as a stable, crystalline compound. These three intermediates, (VII)(VIII) and (IX), serve as convenient starting materials for the synthesis of poly(p-benzenesulphonamide) (III). Of particular interest is the solid state polymerisation of (IX) to give (III). Differential thermal analysis studies revealed an initial exothermic rearrangement reaction at 110°C to give (X), the hydrochloride of the sulphene (V), followed by an endothermic reaction at 165°C, leading to polymer formation with elimination of hydrogen chloride. Dehydrochlorination of (VIII) or (IX) with pyridine also leads to polymer formation.

Treatment of N-acetylsulphanilyl chloride (XI) with pyridine leads to the formation of the water-soluble, acetylated poly(p-benzene-sulphonamide). By a series of trapping experiments, we have been able to establish unequivocally that the reaction proceeds through the intermediate formation of a sulphene

species. This sulphene has been isolated and characterised as the zwitterionic, pyridine adduct:



In the case of the reactions of (VIII) and (IX) with pyridine, the issue of the sulphene intermediacy is somewhat obscured since there is stronger competition between the polymerisation of (V) and its addition reactions.

By melt polymerisation, N-acetylsulphanilic acid, its chloride, ethyl ester and phenyl ester have been converted into polysulphonamides. N-acetylsulphanilic chloride (XI) polymerises with evolution of hydrogen chloride and acetyl chloride to give a copolymer made of units of $\leftarrow NH\text{-}C_6H_4\text{-}SO_2\rightarrow$ and $\leftarrow \underset{\underset{COCH_3}{|}}{N}\text{-}C_6H_4\text{-}SO_2\rightarrow$. An interesting reaction between (XI) and dimethyl formamide has been discovered.

Following the early work of Zincke and Brune[1], there has been considerable speculation about the possible formation of quinonoid sulphene intermediates in the synthesis of polysulphonates of type (VI). Hall[2] has prepared a series of such polymers from 2,5-disubstituted phenol-4-sulphochloride and -sulphofluoride by treatment with base. On the basis of certain ultraviolet studies, he claimed that the yellow colour which is initially formed on additon of base as noted by Zincke and Brune, was due not to sulphene formation but to the generation of the phenolate anion. We have critically examined and extended the work of Hall and have prepared a number of polysulphonates. In the course of these polymerisations, some oligomeric species are also formed. Cyclic disulphonates have been isolated and characterised.

1. Zincke and Brune, Ber., 41, (1908), 902.
2. Hall, J. Org. Chem., 31, (1966), 2672.