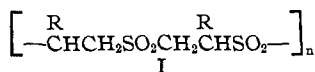


## Structural Identity of Polysulfones Prepared by Peroxide Catalysis and Under the Influence of Ultraviolet Light<sup>1</sup>

BY C. S. MARVEL AND WM. H. SHARKEY

Olefins of the type  $RCH=CH_2$  combine with sulfur dioxide in the presence of peroxides to give polysulfones with the structure shown in formula I.<sup>2</sup> The unusual orientation of the units sug-



gested to us that the peroxides present might be exerting an effect similar to that which has been discovered by Kharasch and his students<sup>3</sup> in connection with the addition of hydrogen bromide to olefins. It has been reported<sup>4</sup> that ultraviolet light promotes the addition of sulfur dioxide to olefins. While previous work in this Laboratory has indicated that it will not induce polymer formation in all cases,<sup>5</sup> we have now found that it does bring about the combination of 1-pentene with sulfur dioxide. This has made it possible for us to compare the structure of 1-pentenepolysulfone prepared with peroxide catalysts with that of the polymer prepared by photochemical activation in the absence of peroxides. The two products apparently are identical and beyond question have the same structural units.

1-Pentene was shaken with concentrated aqueous hydrochloric acid until it gave no test for peroxides with ferrous sulfate and ammonium thiocyanate.<sup>6</sup> The olefin was then distilled and again found to give no test for peroxides. A 5-cc. sample of this peroxide-free olefin and 5 cc. of liquid sulfur dioxide were placed in a Pyrex tube and nitrogen was passed through the tube for about twenty minutes to remove all of the air. The tube was then sealed and placed under an ultraviolet lamp. Evidence of polymer formation was noticed after twenty-four hours. After one week the tube was opened and the polymer was isolated. The yield was 5 to 5.2 g. The polymeric product had the same physical properties and solubilities as reported for the 1-pentenepolysulfone prepared by peroxide catalysts.<sup>2</sup>

(1) This is the ninth communication on The Reaction between Sulfur Dioxide and Olefins. For the eighth see THIS JOURNAL, **60**, 2622 (1938).

(2) Glavis, Ryden and Marvel, *ibid.*, **59**, 707 (1937).

(3) For leading references see Kharasch, Norton and Mayo, *J. Org. Chem.*, **3**, 48 (1938).

(4) Mathews and Elder, British Patent 11,835 (1914); *C. A.*, **9**, 2971 (1915).

(5) Frederick, Cogan and Marvel, THIS JOURNAL, **56**, 1815 (1934).

(6) Kharasch and Mayo, *ibid.*, **55**, 2468 (1933).

Treatment of 3 g. of this polymer with 150 cc. of liquid ammonia as described previously<sup>2</sup> followed by recrystallization of the resulting product from alcohol gave 0.9 g. (30%) of 2,6-di-*n*-propyl-1,4-dithian-*bis*-(dioxide), m. p. 257°. This product was identical with the synthetic product and that formed by the action of liquid ammonia on 1-pentenepolysulfone prepared in the presence of peroxides.<sup>2</sup>

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## The Oxidation of Phenyllithium

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The formation of significant quantities of coupling or R·R compounds by oxidation of RLi compounds of the dibenzofuran series<sup>1</sup> suggested an examination of the oxidation products of phenyllithium. Ether-free phenyllithium was used because we wished to exclude the marked secondary reactions known to take place when ether solutions of arylmagnesium halides are oxidized.<sup>2</sup>

We found that biphenyl and phenol are formed in essentially equal quantities. In addition, a small quantity of *p*-phenylphenol was isolated from each of the oxidation reactions. It is possible that the *p*-phenylphenol may owe its formation to the oxidation of some *p*-phenylphenyllithium formed by metalation of biphenyl, for biphenyl is known to metalate in a para position.<sup>3</sup>

It was also observed that when phenyllithium was allowed to take fire in the air, a pronounced odor of biphenyl accompanied the combustion. Incidentally, the solid phenyllithium, phenylsodium, and phenylpotassium, like the phenylmagnesium halides, show chemiluminescence when oxidized.<sup>4</sup>

Müller and Töpel<sup>5</sup> have just reported on the oxidation of some organolithium compounds. Working in ether solutions, these authors found more biphenyl, but less phenol than we did under our conditions. Their phenylmethylcarbinol arose as a consequence of the usual secondary reaction with ether,<sup>2</sup> and they found no other products. With most of the other aryllithium compounds

(1) Gilman, Cheney and Willis, THIS JOURNAL, **61**, 951 (1939).

(2) Wuyts, *Compt. rend.*, **148**, 930 (1909); Porter and Steele, THIS JOURNAL, **42**, 2650 (1920); Gilman and Wood, *ibid.*, **48**, 806 (1926).

(3) Gilman and Bebb, *ibid.*, **61**, 109 (1939).

(4) Ether solutions of phenyllithium were reported earlier to show chemiluminescence on oxidation [Gilman, Zoellner and Selby, *ibid.*, **54**, 1957 (1932)].

(5) Müller and Töpel, *Ber.*, **72**, 273 (1939).