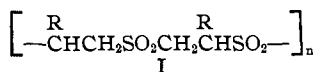


Structural Identity of Polysulfones Prepared by Peroxide Catalysis and Under the Influence of Ultraviolet Light¹

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.² 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 students³ in connection with the addition of hydrogen bromide to olefins. It has been reported⁴ 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,⁵ 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.⁶ 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.²

(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 previously² 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.²

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The Oxidation of Phenyllithium

BY H. A. PACEVITZ AND HENRY GILMAN

The formation of significant quantities of coupling or R·R compounds by oxidation of RLi compounds of the dibenzofuran series¹ 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.²

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.³

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.⁴

Müller and Töpel⁵ 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,² 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).

examined by them, the yield of coupling product was less than that observed with phenyllithium, and in the case of *o*-tolyllithium the yield of bi-*o*-tolyl was 5% and the yield of *o*-cresol, 54%.

Experimental Part

The suspension of 4.5 g. of phenyllithium in 100 cc. of benzene, prepared in a nitrogen atmosphere, was oxidized by dry air, free of carbon dioxide, at 10–15°. A negative color test⁶ was obtained in about ten hours. The phenol was characterized as 2,4,6-tribromophenol, and the *p*-phenylphenol as the acetate.

In three experiments the yields of phenol were 25.9, 23.1, and 22%; of biphenyl, 25, 23.7 and 22.6%; and of *p*-phenylphenol, 0.05, 0.06 and 0.05 g., respectively. The extent of the Wurtz-Fittig reaction with the bromobenzene is quite slight, for only 0.12 g. of biphenyl was isolated from the benzene washings of a 0.1 mole run.

(6) Gilman and Schulze, *THIS JOURNAL*, **47**, 2002 (1925).

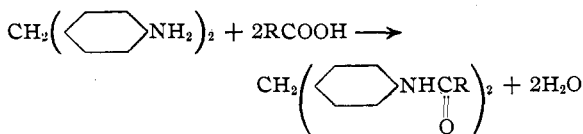
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4,4'-Diaminodiphenylmethane as a Reagent for the Identification of Monobasic Saturated Aliphatic Acids

BY A. W. RALSTON AND M. R. McCORKLE

4,4'-Diaminodiphenylmethane has been found to give diamides of aliphatic acids by heating the theoretical proportions of the diamine with the respective acids.



Because of the ease of preparation and purification and their high melting points, these compounds serve as excellent derivatives for the identification of aliphatic acids. With the lower members there was considerable depression of mixed melting points but this became increasingly smaller as the series was ascended.

In order to establish the structure of the diamides prepared by this method, the diamides of acetic, propionic and lauric acids were prepared from the diamine and either the anhydrides or the acid chlorides. These gave no depression of mixed melting points with the corresponding com-

pounds prepared from the acids. *p,p'*-Methylenbisacetanilide has been prepared previously from acetic anhydride and 4,4'-diaminodiphenylmethane.

Experimental

A mixture of 1 g. (0.005 mole) of 4,4'-diaminodiphenylmethane¹ and slightly more than 0.01 mole of the respective acid were mixed in a large Pyrex test-tube and heated at the boiling temperature until water ceased to be evolved. With the lower members of the series a reflux condenser was used and the period of heating was approximately one hour. The time necessary to complete the reaction decreased with the higher members of the series and in the case of stearic acid five minutes is sufficient. The products were crystallized to a constant melting point from a mixture of benzene and methanol except with some of

TABLE I
CONSTANTS OF DIAMIDES OF 4,4'-DIAMINODIPHENYLMETHANE

Acid	M. p., °C. (corr.)	Mixed m. p. with next highest homolog	N Analyses, %	
			Calcd.	Found
Acetic ^{a,b}	227–228	205–210		
Propionic	212–213	188–193	9.03	9.33
Butyric	197–198	185–188	8.28	8.58
Valeric	188–189	179–181	7.65	7.92
Caproic	185–186	179–181	7.10	7.46
Heptylic	183–184	176–178	6.64	6.86
Caprylic	182–183	176–179	6.22	6.53
Pelargonic	176–177	175–177	5.83	6.11
Capric	178–179	173–175	5.54	5.93
Undecylic	175–176	172–174	5.25	5.45
Lauric ^c	174–175	171–173	4.99	5.38
Tridecylic	172–173	170–172	4.78	5.12
Myristic	170–171	167–169	4.53	4.73
Pentadecylic	167–168	166–168	4.34	4.36
Palmitic	167–168	164–166	4.15	4.39
Margaric	164–165	163–165	3.99	4.40
Stearic	164–165		3.83	4.12

^a In order to purify this sample it was necessary to dissolve it in ethanol and add alkali until basic to phenolphthalein. Upon dilution with water and crystallization from benzene and methanol the product, m. p. 227–228°, was obtained. ^b Stoedel and Hause, *Ber.*, **23**, 2577 (1890); Rivier and Farine, *Helv. Chim. Acta*, **12**, 865 (1929); Parkes and Morley, *J. Chem. Soc.*, 315 (1936); Butler and Adams, *THIS JOURNAL*, **47**, 2617 (1925), reported m. p. 236–237°. ^c The authors are indebted to Mr. W. M. Selby for the samples of lauric, myristic and stearic acids. The remainder of the acids were obtained from the Eastman Kodak Company.

(1) The 4,4'-diaminodiphenylmethane used was prepared by crystallization from petroleum ether of Eastman Kodak Co. (practical), 4,4'-diaminodiphenylmethane, m. p. 90–91.5°. The melting point was 92–93°.