

it other compounds such as nitric oxide, nitromethane, and ethyl or benzyl bromides, which might act as chain breakers, were without avail. On the other hand, cinnamyl bromide was even more effective as an inhibitor than allyl bromide. Two mole per cent. of this compound was sufficient to reduce the yield of allyl chloride polysulfone to less than 3%. The structure $RR_1C=CHCH_2Br$ appears to be a prerequisite for this type of inhibitor. This view is substantiated by the facts that hydrogen bromide is not an inhibitor, and that substances such as trichloroethylene and 2,4,4-trimethylpentene-2 do not form polysulfones, yet neither do they inhibit the formation of a polysulfone from allyl chloride.

Experimental Part

Allyl Chloride Polysulfone.—This compound has been described incompletely by Marvel and Glavis.¹ To 10 cc. of liquid sulfur dioxide in a flask or beaker was added 5 g. of allyl chloride, a drop of ascaridole, and a few drops of aqueous or alcoholic hydrogen chloride, hydrogen bromide, or sulfuric acid. The polysulfone began in a few seconds to precipitate as a white viscous mass which hardened in a minute or two. The reaction was complete in less than five minutes. Ether was added; then the mass was broken up, collected on a filter, powdered, washed thoroughly with ether, and dried; yields, 6.5–9 g. (70–100%). The compound has no melting point but decomposes when heated to 210–235°. It is soluble in acetone and chloroform, but insoluble in most other organic solvents.

Anal. Calcd. for $(C_3H_5SO_2Cl)_n$: C, 25.44; H, 3.53; S, 22.78. Found: C, 25.23; H, 3.96; S, 22.82.

Lauroyl, benzoyl, and hydrogen peroxides were ineffective when used in place of ascaridole. Mineral acids could not be replaced in the reaction by acetic or trichloroacetic acid.

Trimethylethylene Polysulfone.—A solution of 7 g. of trimethylethylene, 10 cc. of sulfur dioxide, 0.2 cc. of ascaridole, and 3 g. of hydrogen bromide was allowed to stand in a pressure bottle for twelve hours at room temperature. The bottle was opened, the dark viscous mass dissolved in chloroform, and the polysulfone precipitated with ether. It was dried, powdered, washed thoroughly with ether, and dried again; yield, 6 g. of a dark powder (44%). It melts with decomposition at 125–160°.

Anal. Calcd. for $(C_5H_{10}SO_2)_n$: C, 44.74; H, 7.46; S, 23.89. Found: C, 43.54; H, 7.17; S, 24.36.

A large quantity of halogen acid, 50 mole per cent., was found to be necessary for the formation of trimethylethylene polysulfone. Ascaridole was the only peroxide that brought about the reaction.

Vinyl Chloride Polysulfone.—This compound, described by Marvel and Glavis,¹ was obtained by adding aqueous hydrogen chloride or bromide to a solution of vinyl chloride in sulfur dioxide containing a trace of ascaridole; yield, 50%. The substance decomposes when heated at 245–265°.

Summary

1. The combined effect of acid and peroxides on polysulfone formation of olefins and sulfur dioxide has been studied.

2. It was shown that allyl and cinnamyl bromides do not form polysulfones and act as inhibitors in polysulfone formation from other olefins.

3. Allyl chloride and trimethylethylene polysulfones are described.

JONES CHEMICAL LABORATORY
THE UNIVERSITY OF CHICAGO
CHICAGO, ILLINOIS

RECEIVED JULY 20, 1940

Condensation of Sulfanilamide with an Enol. N^4 - α -Bromotetronyl Sulfanilamide¹

BY W. D. KUMLER

Sulfanilamide reacts with α -bromotetronic acid when the solid compounds are ground together in a mortar and heated at 110–120°. The original white powder turns red, partially melts and then solidifies. After three crystallizations from 50% acetone-water, a colorless or cream colored compound occurring as fine silky needles was obtained.

Other ways of bringing about the reaction were tried including refluxing the solids while suspended or dissolved in glacial acetic acid, anhydrous dioxane, and toluene. The best results were obtained with toluene. When equal molal quantities of sulfanilamide and α -bromotetronic acid were placed in toluene and refluxed for two hours, a 31% yield of the purified product was obtained.

Sulfanilamide and α -bromotetronic acid might react in several ways. The possibilities are: salt formation, cleavage of hydrogen bromide (the hydrogen coming from either the amino or the amide nitrogen), cleavage of water, the hydrogen again coming from either the amino or amide nitrogen.

The molecular weight of the compound was determined in acetone using a Reiche apparatus. Values of 319, 330 and 329 were obtained which are near the theoretical value of 333 for the molecule formed by splitting out of water. The theoretical molecular weight for the compound formed by splitting out hydrogen bromide is 270 and that for the salt assuming ionization is 176. The compound has a low solubility in water, which would not be the case if it were a simple salt.

(1) Presented before the Division of Medicinal Chemistry at the Cincinnati meeting of the American Chemical Society, April 11, 1940.

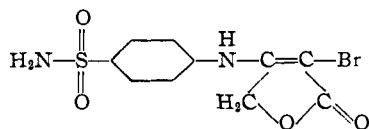
The bromine observed was 24.11 and 23.86, in good agreement with the theoretical value of 24.00 for the compound formed by splitting out water.

The two possibilities are then N^4 - α -bromotetronyl sulfanilamide and N^1 - α -bromotetronyl sulfanilamide. The N^1 -compound would be analogous to a secondary sulfonamide since α -bromotetronic acid is a strong acid pK_a 2.23,² and such a sulfonamide would be sufficiently acidic to titrate accurately to the phenolphthalein end-point. On the other hand, the N^4 -compound would have very weak acidic properties. Our compound has very weak acidic properties and gives a very high equivalent weight at the phenolphthalein end-point.

The N^1 -compound would likewise be expected to undergo diazotization at 0°, couple and give a bright color with alkaline α -naphthol, while the N^4 -compound would not give a color. Our compound gives no color other than a pale yellow, which was also obtained with a blank. The compound can, however, be hydrolyzed in either 10% hydrochloric acid or 10% sodium hydroxide to give a compound that gives the test for a primary aromatic amine group.

An attempt was made to condense α -bromotetronic acid with a compound in which the amino group in sulfanilamide was blocked, N^4 -acetylsulfanilamide. The same conditions were used that gave the best results with sulfanilamide but no evidence of any reaction was obtained and 90% of the N^4 -acetylsulfanilamide was recovered unchanged.

The evidence from all sources indicates that the compound is N^4 - α -bromotetronyl sulfanilamide.



This compound is of interest because it is a new type of sulfanilamide derivative formed by condensing an enol with sulfanilamide. The compound has a possible tautomeric form but the structure given is the more likely one due to the stability resulting from the resonance forms that are possible with it but not with its tautomer.

Preliminary investigation of the pharmacology of the compound in Dr. Chauncey D. Leake's laboratory in the University of California Medi-

cal School indicates that the compound has a very low toxicity. Twelve grams per kilo of body weight were given orally to mice without any fatalities. The compound has a protective action against β -hemolytic streptococcus that is about equal to that of sulfanilamide.

COLLEGE OF PHARMACY
UNIVERSITY OF CALIFORNIA
SAN FRANCISCO, CALIFORNIA

RECEIVED JUNE 11, 1940

The Quantitative Analysis of Mixtures of Polyoxyethylene Glycols by Fractional Distillation¹

BY STANLEY PERRY AND HAROLD HIBBERT

A method for the quantitative separation of the products of hydrolysis of methylated polysaccharides by fractional distillation has been used with some success by Haworth and co-workers² in molecular weight determinations by the end-group method. More recently, Hess³ has modified the method so as to make it even more sensitive for the determination of tetramethyl methyl glucoside. However, the efficacy of a distillation analysis of this type is not very generally recognized, so that it is of some interest that a similar accurate separation has now been found possible with complex mixtures of polyoxyethylene glycols, $\text{HOH}_2\text{C}(\text{CH}_2\text{OCH}_2)_n\text{CH}_2\text{OH}$. Thus, the quantitative separation of these liquid polymers has been obtained by subjecting synthetic mixtures to fractional distillation, the course of the separation being followed in each case by the change in refractive index of the distillate.

The applicability of the process to the separation of unknown mixtures was fully established by collaborative experimentation, the senior author preparing synthetic mixtures which were then separated into their components by the junior author, who was not informed of the number or proportions. Under these conditions, it was not only possible to detect which members were present and which were not, but also to isolate and determine quantitatively the proportion of each with an accuracy of 96 to 99.8%. This is illustrated in the accompanying tables of data.

The mixtures used in these experiments were prepared from carefully purified products pre-

(1) Part LX of the series "Studies on Reactions Relating to Carbohydrates and Polysaccharides."

(2) Haworth and Macheimer, *J. Chem. Soc.*, 2270 (1932); Haworth and Percival, *ibid.*, 2277 (1932).

(3) Hess and Neumann, *Ber.*, 70B, 710 (1937).

(2) Kumler, *This Journal*, 60, 859 (1938).