mm. and a temperature in the still of 100 to 150°. The gelatinous precipitate that separated was removed by filtration at an early stage in the distillation. After being washed with ethanol and ether and dried to constant weight in a vacuum desiccator, it weighed 1.17 g., or about 0.09% of the original weight. On ignition the precipitate gave 19.7% ash (calcd. for $C_{20}H_{20}O_4Zn$, 20.8% ZnO). The ash gave qualitative tests for zinc. Another portion of the dried precipitate, after being suspended in water, acidified with dilute sulfuric acid, and extracted with ether, gave after removal of the solvent a white crystalline solid. After several recrystallizations from dilute ethanol it melted at 106°.[2] In ethanol solution the compound gave a deep blue color with ferric chloride. When it was mixed with a sample of pure bieugenol prepared from eugenol by the method of Erdtman,[3] there was no depression of the melting point. On catalytic hydrogenation in ethanol with Adams platinum oxide as catalyst, it was readily reduced with the formation of tetrahydrobieugenol, which after recrystallization from ethanol melted at 151°. Erdtman gives 152° as the melting point of this compound.

Eugenol.—A portion (178 g.) of that fraction of the crude geraniol remaining after three-fourths by volume had been distilled was diluted with ether and extracted with 5% aqueous sodium carbonate and then with 5% aqueous sodium hydroxide. The latter extract was acidified and extracted with ether. The water-washed ether extract was dried over sodium sulfate. After removal of the ether, there remained 4.5 g. of oil having a clove-like odor. It was purified by distillation under reduced pressure. It distilled at 142–142.5° (23.5 mm.). The distillate ($n^{30}\text{D}$ 1.5345) gave a deep blue color with ferric chloride. The 3,5-dinitrobenzoate prepared by the method of Phillips and Keenan[4] had a melting point of 130.5°. A mixture with the 3,5-dinitrobenzoate of eugenol gave no depression of the melting point.

The original sample of crude geraniol gave 1.8% total material soluble in 5% sodium hydroxide.

Zinc in Water Washings.—Crude geraniol (445 g.) was diluted with ether and extracted with water. When the water solution had been evaporated practically to dryness, 0.5 g., or about 0.1%, of material was obtained. On ignition an ash was obtained which gave qualitative tests for zinc. A portion of the water-soluble solid was acidified and extracted with ether. The evaporated extract gave no color with ferric chloride.

A portion of the water-insoluble crude geraniol from the water washing gave no precipitate when boiled for about fifteen minutes. A similar portion of the original unwashed crude geraniol gave a voluminous, gelatinous precipitate after boiling for about two minutes.

Bieugenol in Residue from Steam Distillation.—A portion of the crude geraniol (888 g.) was subjected to steam distillation until about 95% by weight had distilled. The residue was extracted with ether, and the ether solution was extracted successively with 5% aqueous solutions of potassium bicarbonate, sodium carbonate and sodium hydroxide. The final extract yielded, after acidification, extraction with ether and removal of the solvent, a product consisting of crystalline material and a brown, viscous oil. The yield was 0.84 g. (about 0.1% of the sample). The mixture was washed with dilute ethanol, and the crystalline residue was recrystallized several times from the same solvent. The product melted at 106° and showed no depression of melting point in admixture with bieugenol prepared by the method of Erdtman.[3]

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[2] All melting points are corrected.

[3] Erdtman, *Biochem. Z.*, **258**, 172 (1933).

[4] Phillips and Keenan, THIS JOURNAL, **53**, 1924 (1931).

Factors Influencing Polysulfone Formation

BY M. S. KHARASCH AND E. STERNFELD

In the course of an investigation involving sulfur dioxide and olefins we were concerned with the possibility of polysulfone formation as an undesirable side reaction. We found that mineral acids, in the presence of a peroxide such as ascaridole, markedly catalyzed this reaction for several olefins which did not readily form polysulfones. Recently, Marvel and Glavis[1] have found peracetic acid a more potent catalyst than acyl peroxides in the formation of polysulfones from vinyl and allyl chlorides. From our experiments, it would seem that a mixture of ascaridole and hydrochloric, hydrobromic, or sulfuric acid is at least as effective as peracetic acid in polysulfone formation from trimethylethylene and allyl or vinyl chlorides.

Allyl bromide does not give a polysulfone under any conditions. What is more remarkable, we found it to be a powerful inhibitor for the formation of polysulfones from other olefins. Thus, allyl chloride mixed with five mole per cent. of allyl bromide does not react to any extent with sulfur dioxide even in presence of ascaridole and mineral acid, whereas without the allyl bromide the yield of allyl chloride polysulfone is practically quantitative. A large excess of ascaridole over the allyl bromide (10 moles to 1) brought about the formation of allyl chloride polysulfone. The yield, however, was poor (less than 20%). Allyl bromide was also a powerful inhibitor for polysulfone formation from cyclohexene and pentene-2 when (following the procedure of Frederick, Cogan and Marvel[2]) aqueous hydrogen peroxide was used as a catalyst. In these cases, the addition of mineral acids overcame this inhibition.

It is difficult to explain the action of allyl bromide as an inhibitor. Attempts to substitute for

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[1] Marvel and Glavis, *ibid.*, **60**, 2622 (1938).

[2] Frederick, Cogan and Marvel, *ibid.*, **56**, 1815 (1934).

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.

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Condensation of Sulfanilamide with an Enol. N⁴-α-Bromotetronyl Sulfanilamide[1]

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.

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