

a linear variation of γ_0 with P although, as might be expected from the result discussed previously, the 186-membered glycol does not fit the curve.

To further establish the validity of this wider generalization, the precipitability results of Staudinger and Heuer⁸ for the hemicolloidal polystyrenes are included in Fig. 6. It is obvious from these curves that both types of polymers conform to this simple relationship.

Conclusion.—A point of interest in connection with the above experiments is the significance of the $\log c-\gamma$ slope changes as the higher degrees of polymerization are reached. It is customary to fractionate mixtures of polymer homologous compounds by successive additions of some precipitant to a solution of the mixture, the higher members being first precipitated and followed in order by the lower members as the precipitant concentration is increased.⁹

However, if the concentrations and nature of solvents used are such that the situation expressed in Fig. 3 exists, the results of such a fractionation would be unlikely to lead to the simple separation of high and low members expected. Indeed, the literature contains not a few examples of fractional precipitations which have apparently resulted in the low molecular weight members being precipitated first,¹⁰ but little attention seems to have been

(9) Schulz, *Z. physik. Chem.*, **B32**, 27 (1936).

(10) See, for example, Okamura, *Cellulosechemie*, **14**, 135 (1933); Glückmann, *Kolloid-Z.*, **76**, 84 (1936).

paid to this fact. The importance of obtaining as nearly uniform polymers (in chain length) as possible in studies of the macromolecular state points to the advantage and desirability of *quantitative* studies of precipitation and fractionation phenomena.

Summary

1. The relationships between the precipitability, solubility and degree of polymerization of a number of pure long-chain polyoxyethylene glycols have been determined in methanol-ether and dioxane-ether mixtures.

2. For each glycol, the logarithm of the solubility (in per cent.) was found to be a linear function of the percentage of precipitant (ether) in the mixed solvent methanol-ether.

3. An anomalous behavior of the 186-membered glycol, in this respect, is recorded, and its possible significance for the customary methods of fractionation of higher polymers, especially those of a micro-crystalline character, is pointed out.

4. The experimental results have been compared with those of other authors on polystyrene polymers, and certain theoretical and actual differences indicated. A new generalization relating the precipitability factor to the degree of polymerization is suggested, which brings both these sets of results into general agreement.

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NOTES

The Crystal Structure of Synthetic Antimony Trisulfide

BY HAROLD P. KLUG AND G. B. HEISIG

Red (orange) and black varieties of antimony trisulfide have been prepared in various ways from very early times, and likewise occur in nature.¹ The red variety has been regarded as amorphous, while the black variety is crystalline and reported to be identical with the mineral stibnite, Sb_2S_3 , except in sp. gr.¹ Stibnite has been investigated

(1) Mellor, "Comprehensive Treatise on Inorganic and Physical Chemistry," Vol. IX, Longmans, Green and Co., New York, 1929, p. 512.

by several workers,² but no one seems to have reported X-ray observations on the artificial sulfides. Recently we have been interested in the two varieties of antimony trisulfide as prepared in the laboratory, and have examined them with X-rays. The results are in accord with earlier observations by other methods, and we report them primarily as a matter of record.

Red antimony trisulfide was prepared by passing a current of hydrogen sulfide through a hydrochloric acid solution of antimony trichloride

(2) See for example: Gottfried, *Z. Krist.*, **65**, 428 (1927); Gottfried and Lubberger, *ibid.*, **71**, 257 (1929); Hoffmann, *ibid.*, **86**, 225 (1933).

containing tartaric acid. The red variety was converted into the black variety by heating at 115°.

X-Ray powder photographs were taken at room temperature using CuK and FeK radiation. The above red product, and a sample of the red sulfide from Kahlbaum, both gave photographs showing absolutely no evidence of a crystalline nature. The black variety prepared above gave a pattern identical with that of stibnite, both as to position and intensity of the lines, indicating that there could be little if any amorphous material in the product.

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Sulfonic Acid Esters of 4,4'-Dihydroxydiphenyl

BY STEWART E. HAZLET

In connection with some other work in progress in this Laboratory a number of aryl sulfonic acid esters of 4,4'-dihydroxydiphenyl have been prepared. The method of preparation used was the same as that previously reported¹ except that the phenol (5 g.) was treated with 2.1 molecular proportions of the necessary acid chloride. The crystalline products were colorless except in the case of the *m*-nitrobenzenesulfonate, which was obtained as tan flakes. Of the esters, the benzene- and the *o*-nitrobenzenesulfonyl derivatives are best suited for use as derivatives for the identification of the phenol, for they are the ones most readily purified. The experimental results are summarized in Table I.

TABLE I
SULFONIC ACID ESTERS OF 4,4'-DIHYDROXYDIPHENYL

Sulfonyl chloride used	Solvent	Yield, ^a %	M. p., °C.	Formula	Analyses, %	
					Calcd.	Found
Benzene	<i>n</i> -PrOH	89	148	C ₂₄ H ₁₈ O ₆ S ₂	S, 13.73	13.97
<i>p</i> -Toluene	<i>n</i> -PrOH	Quant.	187-188 ^b	C ₂₆ H ₂₂ O ₆ S ₂		
<i>o</i> -Nitrobenzene	Gl. AcOH	Quant.	191-192	C ₂₄ H ₁₆ O ₁₀ N ₂ S ₂	S, 11.51	11.93
<i>m</i> -Nitrobenzene	Cyclohexanol	Quant.	216-217	C ₂₄ H ₁₆ O ₁₀ N ₂ S ₂	S, 11.51	11.51
<i>p</i> -Nitrobenzene	1,4-Dioxane	87	231	C ₂₄ H ₁₆ O ₁₀ N ₂ S ₂	S, 11.51	11.44
<i>p</i> -Bromobenzene	^c	Quant.	201-202	C ₂₄ H ₁₆ O ₆ Br ₂ S ₂	Br, 25.64	25.98

^a Crude product. ^b This compound was prepared by Gilman, Beaber and Myers [THIS JOURNAL, 47, 2047 (1925)] by treating the phenol with the acid chloride in the presence of potassium hydroxide. Benzene was used for crystallization and a product melting at 189-190° was obtained in 21.2% yield. ^c The compound was first dissolved in acetone and then precipitated by the addition of water; it was purified by crystallization from cyclohexanol and finally by washing with ethanol.

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(1) Hazlet, THIS JOURNAL, 59, 287 (1937).

Sterols. LXVII. Sarsasapogenin Derivatives. Bromo Compounds

BY RUSSELL E. MARKER AND EWALD ROHRMANN

In a preceding paper¹ of this series the reaction of sarsasapogenin acetate with bromine to yield a monobromo derivative of the composition C₂₉-H₄₅O₄Br was described. We have made several additional observations which are of interest concerning the nature of the bromo compounds.

The great ease of bromination of sarsasapogenin and its derivatives is exemplified by the fact that sarsasapogenone reacts with one mole of bromine to give a compound which is identical with the compound formed when bromosarsasapogenin is oxidized at 25° with chromic anhydride.

The bromo compounds are peculiar in that they appear to be unaffected by boiling with pyridine or by treatment with pyridine and silver nitrate in the cold. The bromine is, however, easily eliminated by other reactions. Catalytic hydrogenation of bromosarsasapogenin acetate in hot acetic acid followed by hydrolysis gave a rather poor yield of dihydrosarsasapogenin.¹ Treatment of bromosarsasapogenin acetate with sodium and amyl alcohol gave a good yield of sarsasapogenin. Similar results were obtained with sodium and ethanol. Treatment of bromosarsasapogenin acetate with zinc dust and acetic acid gave sarsasapogenin acetate. Attempts to hydrolyze the bromo compounds with potassium acetate were unsuccessful, non-crystalline mixtures being obtained. Bromosarsasapogenin, upon Clemmensen reduction in alcohol solution with amalgamated zinc, gave a good yield of tetrahydrosarsasapogenin.

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(1) Marker and Rohrmann, *ibid.*, 61, 846 (1939).