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 Heuer[3] 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–γ 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 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.

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

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

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.

MONTREAL, CANADA RECEIVED MAY 3, 1939

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 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

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

(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.

SCHOOL OF CHEMISTRY
UNIVERSITY OF MINNESOTA
MINNEAPOLIS, MINNESOTA

RECEIVED MAY 26, 1939

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 reported[1] 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	*n*-PrOH	89	148	$C_{24}H_{18}O_6S_2$	S, 13.73	13.97
p-Toluene	*n*-PrOH	Quant.	187–188[b]	$C_{26}H_{22}O_6S_2$		
o-Nitrobenzene	Gl. AcOH	Quant.	191–192	$C_{24}H_{16}O_{10}N_2S_2$	S, 11.51	11.93
m-Nitrobenzene	Cyclohexanol	Quant.	216–217	$C_{24}H_{16}O_{10}N_2S_2$	S, 11.51	11.51
p-Nitrobenzene	1,4-Dioxane	87	231	$C_{24}H_{16}O_{10}N_2S_2$	S, 11.51	11.44
p-Bromobenzene	[c]	Quant.	201–202	$C_{24}H_{16}O_6Br_2S_2$	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.

DEPARTMENT OF CHEMISTRY
STATE COLLEGE OF WASHINGTON
PULLMAN, WASHINGTON

RECEIVED MAY 8, 1939

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

Sterols. LXVII. Sarsasapogenin Derivatives. Bromo Compounds

BY RUSSELL E. MARKER AND EWALD ROHRMANN

In a preceding paper[1] of this series the reaction of sarsasapogenin acetate with bromine to yield a monobromo derivative of the composition $C_{29}H_{45}O_4Br$ 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.

We wish to thank Parke, Davis and Company for their generous support and assistance in the various phases of this work.

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

Experimental Part

Bromosarsasapogenin.—A solution of 820 mg. of sarsasapogenin in 50 cc. of glacial acetic acid was cooled to 20°. Two drops of 48% hydrobromic acid was added and 2.1 cc. of 1.05 *M* bromine in acetic acid solution run in dropwise. The bromine was taken up readily with the liberation of hydrogen bromide. The mixture was poured into water and the precipitated solid collected and washed with water. The residue was crystallized from aqueous acetone to give white needles which began to decompose at about 125°.

Anal. Calcd. for $C_{27}H_{43}O_3Br$: C, 65.4; H, 8.8. Found: C, 65.1; H, 8.8.

In carrying out the bromination of sarsasapogenin derivative on a somewhat larger scale (5–10 g.) the reaction mixture often became deep blue in color.

Bromosarsasapogenone from Bromosarsasapogenin.—To a solution of 100 mg. of bromosarsasapogenin in 50 cc. of glacial acetic acid was added 300 mg. of chromic anhydride in 10 cc. of 80% acetic acid. After standing at room temperature for forty minutes the mixture was poured into water, the precipitated material was extracted with ether and the ethereal extract washed with sodium carbonate solution and water. The ether was evaporated on the steam-bath and the residue crystallized from acetone to give pale tan crystals, m. p. 191° dec. This gave no depression with a sample of bromosarsasapogenone prepared by the direct bromination of sarsasapogenone.

Anal. Calcd. for $C_{27}H_{41}O_3Br$: C, 65.7; H, 8.4. Found: C, 65.3; H, 8.3.

Bromination of Sarsasapogenone.—Sarsasapogenone was treated with bromine as described in the preceding experiments. The material was crystallized from acetone to give white crystals, m. p. 190° dec. The material evidently was contaminated with some of the dibromo compound as is shown by the analysis. The material gave no depression with the product obtained in the preceding experiment.

Anal. Calcd. for $C_{27}H_{41}O_3Br$: C, 65.7; H, 8.4. Found: C, 65.1; H, 8.0.

Reduction of Bromosarsasapogenin Acetate. (a) **With Zinc and Acetic Acid.**—To a solution of 500 mg. of bromosarsasapogenin acetate in 50 cc. of glacial acetic acid heated on the steam-bath was added with shaking 3 g. of zinc dust in small portions over a period of twenty minutes. White crystals had separated out at the end of this time. The mixture was poured into water and extracted with ether. The ethereal extract was washed first with sodium carbonate solution and then with water. Evaporation of the ethereal solution gave a crystalline residue which was crystallized from acetone to give white needles, m. p. 142°; yield 250 mg. This gave no depression with an authentic sample of sarsasapogenin acetate. The mother liquors yielded some unchanged bromosarsasapogenin acetate.

(b) **With Sodium and Amyl Alcohol.**—To a boiling solution of 700 mg. of bromosarsasapogenin acetate in 50 cc. of *n*-amyl alcohol was added 2.5 g. of sodium in small pieces over a period of two hours. The mixture was cooled and shaken first with an excess of dilute hydrochloric acid and then with water. The amyl alcohol was evaporated on the steam-bath and the residue, after treatment with Norite, was crystallized from acetone to give white needles of sarsasapogenin, m. p. 197°, which gave no depression with an authentic sample.

Similar results were obtained with sodium and absolute ethanol.

(c) **By Catalytic Hydrogenation.**—A mixture of 1 g. of bromosarsasapogenin acetate, 0.5 g. of Adams catalyst, and 80 cc. of glacial acetic acid was shaken with hydrogen at 3 atmospheres and 70° for eight hours. The mixture was filtered and the filtrate evaporated *in vacuo*. The oily residue was diluted with water and the mixture extracted with ether. The ethereal solution was washed with water and the ether evaporated. The residue would not crystallize; it was refluxed for fifteen minutes with an excess of alcoholic potassium hydroxide, poured into water and extracted with ether. The ethereal extract was washed with water and the ether evaporated on the steam-bath. The residue was crystallized from ether–pentane to give white needles, m. p. 163°. This gave no depression with a sample of dihydrosarsasapogenin. The yield was rather poor and the mother liquors contained brominated products.

Anal. Calcd. for $C_{27}H_{46}O_3$: C, 77.4; H, 11.1. Found: C, 77.3; H, 11.2.

(d) **By Clemmensen Reduction.**—Reduction of 500 mg. of the bromoacetate by the Clemmensen method, as described in a previous paper for sarsasapogenin acetate gave a product which crystallized from acetone as compact white crystals, m. p. 191°; yield 375 mg. This gave no depression with an authentic sample of tetrahydrosarsasapogenin, m. p. 193°.

(e) **Treatment with Pyridine.**—Treatment of bromosarsasapogenin acetate with boiling pyridine for twelve hours did not remove the bromine. Treatment with pyridine and silver nitrate at 25° for twenty-four hours was likewise without effect on the substance.

Dibromosarsasapogenone.—To a solution of 7 g. of sarsasapogenone in 350 cc. of glacial acetic acid was added 5 drops of 48% hydrobromic acid and 33.8 cc. of 1.05 *M* bromine in glacial acetic acid was slowly run in over a period of forty minutes at room temperature. The solution became intensely blue and much hydrogen bromide was liberated. The solution was poured into 2 liters of water and the precipitate collected and washed with water. The dried material was crystallized from acetone–ethyl acetate to give small compact white crystals, m. p. 190° dec.

Anal. Calcd. for $C_{27}H_{40}O_3Br_2$: C, 56.7; H, 7.1. Found: C, 57.2; H, 7.3.

SCHOOL OF CHEMISTRY AND PHYSICS
THE PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PENNA. RECEIVED APRIL 1, 1939

Sterols. LXVIII. Highly Branched Aliphatic Esters of Estrone and α-Estrodiol

BY RUSSELL E. MARKER AND EWALD ROHRMANN

The trimethylacetates and the *t*-butylacetates of estrone and α-estrodiol were prepared by the

reaction of these compounds with the corresponding acid chlorides in pyridine. Catalytic hydrogenation of the estrone derivatives in neutral medium yielded the mono esters of α-estrodiol. Estrone *t*-butylacetate was also prepared by the Schotten–Baumann procedure. The esters prepared appear to be somewhat more soluble than are many of the other well known esters of these substances.

We wish to thank Parke, Davis and Company for their generous help and assistance in the various phases of this work.

Experimental Part

Estrone Trimethylacetate.—To a solution of 300 mg. of estrone in 12 cc. of dry pyridine was added 1 cc. of trimethylacetyl chloride. The resulting mixture, after standing at room temperature for thirty-six hours, was diluted with water and the precipitated solid taken up in ether. The ethereal extract was washed with dilute hydrochloric acid and dilute sodium carbonate solution. Evaporation of the ether gave white needles which was recrystallized from acetone–methanol as thick white needles, m. p. 164–166°.

Anal. Calcd. for $C_{23}H_{30}O_3$: C, 77.9; H, 8.5. Found: C, 77.6; H, 8.3.

α-Estrodiol-3-trimethylacetate.—A mixture of 200 mg. of estrone trimethylacetate, 300 mg. of Adams catalyst, 50 cc. of ether and 50 cc. of ethanol was shaken with hydrogen at 1 atmosphere pressure at room temperature for eighteen hours. The mixture was filtered and the filtrate evaporated *in vacuo*. The residual sirup was treated with Norite and crystallized from aqueous methanol as white needles, m. p. 178–180°.

Anal. Calcd. for $C_{23}H_{32}O_3$: C, 77.5; H, 9.0. Found: C, 77.7; H, 9.0.

α-Estrodiol-3,17-*bis*-trimethylacetate.—A mixture of 100 mg. of α-estrodiol, 10 cc. of pyridine and 0.5 cc. of trimethylacetyl chloride was treated as described for the preparation of estrone trimethylacetate. The product was crystallized from acetone–methanol as white needles, m. p. 174–176°.

Anal. Calcd. for $C_{28}H_{40}O_4$: C, 76.3; H, 9.15. Found: C, 76.0; H, 9.2.

Estrone *t*-Butylacetate.—Estrone *t*-butylacetate was prepared by the pyridine method as described for estrone trimethylacetate. The product was crystallized from methanol as white plates, m. p. 148–150°.

Anal. Calcd. for $C_{24}H_{32}O_3$: C, 78.2; H, 8.7. Found: C, 78.1; H, 8.6.

To a solution of 50 mg. of estrone in 150 cc. of 10% aqueous potassium hydroxide was added 1 cc. of *t*-butylacetyl chloride. The mixture was shaken vigorously for five minutes, and the solid collected, washed and dried. The product crystallized from methanol as white plates, m. p. 147.5–149.5°. This gave no depression with that prepared above.

α-Estrodiol-3-*t*-butylacetate.—This was prepared as described for α-estrodiol-3-trimethylacetate. The product was crystallized from aqueous methanol as white needles, m. p. 127–129°.

Anal. Calcd. for $C_{24}H_{34}O_3$: C, 77.8; H, 9.2. Found: C, 78.1; H, 9.4.

α-Estrodiol-3,17-di-*t*-butylacetate.—This was prepared from α-estrodiol as described for α-estrodiol-3,17-*bis*-trimethylacetate. The product was crystallized from methanol as white plates, m. p. 98–100°.

Anal. Calcd. for $C_{36}H_{44}O_4$: C, 76.9; H, 9.5. Found: C, 76.9; H, 9.5.

SCHOOL OF CHEMISTRY AND PHYSICS
THE PENNSYLVANIA STATE COLLEGE
STATE COLLEGE, PENNA. RECEIVED APRIL 28, 1939

COMMUNICATIONS TO THE EDITOR

THE ANTIHEMORRHAGIC ACTIVITY OF CERTAIN NAPHTHOQUINONES

Sir:

We have briefly reported on the antihemorrhagic activity of phthiocol, 2-methyl-3-hydroxy-1,4-naphthoquinone, the first completely identified form of vitamin K [THIS JOURNAL, **61** 1611 (1939)]. Phthiocol has been isolated as the pigment of *Mycobacterium tuberculosis* (human) and synthesized by Anderson and co-workers [*J. Biol. Chem.*, **101,** 773 (1933); **103,** 197 (1933); **105,** 279 (1934)]. This organism is known to contain vitamin K [*Proc. Soc. Exp. Biol. Med.*, **38,** 336 (1938)].

Treatment of vitamin K concentrates with sodium methylate produces a reddish pigment the quantity of which is proportional to the activity of the concentrate [THIS JOURNAL, **61,** 1610 (1939)]. The pigment has a strong red color in alkaline media, from which it can be extracted by adding hexane or ethyl ether and acidifying. It then assumes a yellow color. These color changes of the derived pigment are very similar to those exhibited by phthiocol and similarly