of dry acetone was treated with 4 g. (0.028 mole) of methyl iodide and 4 g. of anhydrous potassium carbonate and the mixture was heated under reflux for 8 hr. on a water bath. The acetone was then evaporated and water was added to the residue. The solid obtained was recrystallized from ethanol; yield, 0.8 g. (54%), m.p. 224–226°.

Anal. Calcd. for $C_{17}H_{15}NO_2S$: C, 68.64; H, 5.08. Found: C, 68.47; H, 5.15.

Di-p-bromophenacyl sulfone. A solution of 15 g. (0.035 mole) of di-*p*-bromophenacyl sulphide[2] in 50 ml. of glacial acetic acid was treated with 25 ml. of 30% hydrogen peroxide. The mixture was heated on a water bath for 2 hr. and cooled in ice water. The solid that separated was removed by filtration and washed with ethanol. After recrystallization from glacial acetic acid, the compound melted at 201–202°. The yield was 8.5 g. (53%).

Anal. Calcd. for $C_{16}H_{12}Br_2O_4S$: C, 41.75; H, 2.63. Found: C, 42.00; H, 2.50.

3,5-Di-p-bromophenyl-1,4-thiazine 1,1-dioxide. A mixture of 1.5 g. (0.00326 mole) of the above sulfone and 0.4 g. (0.0052 mole) of ammonium acetate in 4 ml. of glacial acetic acid was heated under reflux for 5 hr. The mixture was then cooled, the separated solid was filtered and washed with water. Recrystallization from glacial acetic acid gave colorless plates melting at 333° dec. The yield was 1.25 g. (87%).

Anal. Calcd. for $C_{16}H_{11}Br_2NO_2S$: C, 43.57; H, 2.51. Found: C, 43.54; H, 2.70.

Di-p-chlorophenacyl sulfone. Di-*p*-chlorophenacyl sulfide,[3] on oxidation with 30% hydrogen peroxide, gave this sulfone in 53% yield. On recrystallization from ethanol colorless needles melting at 182–183° were obtained.

Anal. Calcd. for $C_{16}H_{12}Cl_2O_4S$: C, 51.76; H, 3.26. Found: C, 51.44; H, 3.37.

3,5-Di-p-chlorophenyl-1,4-thiazine 1,1-dioxide was prepared similarly to 3,5-di-*p*-bromophenyl-1,4-thiazine 1,1-dioxide. The yield was 83%. The compound crystallized from glacial acetic acid as colorless plates and melted at 318–320° dec.

Anal. Calcd. for $C_{16}H_{11}Cl_2NO_2S$: C, 54.56; H, 3.15. Found: C, 54.46; H, 3.14.

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[2] A. Chrzaszczewska and S. Chwalinski, *Roczniki Chem.*, **8**, 432 (1928); *Chem. Abstr.*, **23**, 1629^8 (1929).

[3] A. Chrazaszczewska and S. Chwalinski, *Roczniki Chem.*, **7**, 6773 (1927); *Chem. Abstr.*, **22**, 1339^1 (1928).

Poly(methylene Sulfide)[1]

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Poly(methylene sulfide), also referred to as poly(thioformaldehyde), was synthesized in the course of investigating the relative influence of oxygen and sulfur on the properties of polymers having the repeat units polymethylene oxide and polymethylene sulfide.

EXPERIMENTAL

Synthesis. Into a three-necked 250-ml. flask fitted with a reflux condenser and a mechanical stirrer was added a solution of 43.2 g. (0.18 mole) of sodium sulfide nonahydrate in 80 ml. of water and 20 ml. of 95% ethyl alcohol. The solution was heated to a gentle reflux and 23.6 g. (0.18 mole) of freshly distilled bis(chloromethyl) sulfide,[2] n_D^{29} 1.5301, was gradually added in 15 min. The reaction mixture was refluxed for an additional 2 hr. The precipitated polymer was filtered from the hot reaction mixture, washed free of salts with warm water and finally washed with alcohol and hot benzene. The yield of the vacuum-dried, light yellow, powdery material was 4.9 g. (59.2%). It had a melting temperature[3] range of 220–245° (lit. m.p. 123–124,[4] 175–176).[5,6] These differences in the melting temperature may perhaps be due to differences in the molecular weights of the polymers.

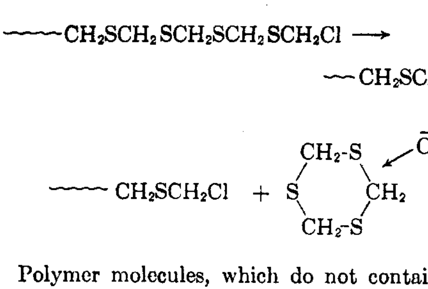
Anal. Calcd. for CH_2S: S, 69.56. Found: S, 68.7.

Properties. The polymer gave a crystalline x-ray diffraction pattern having *d* values of 4.37 (strong), 3.19 (weak), 3.00 (medium), 2.53 (weak), and 2.17A (weak).

It was insoluble in the boiling solvents: benzene, dioxane, *o*-dichlorobenzene, *N,N*-dimethylformamide, and nitromethane. Its reported solubility in alcohol and ether[4] or dimethylformamide[5] is contrary to our observations. The polymer was, however, soluble in *o*-phenylphenol and mixed tetrachlorobiphenyl (Monsanto's "Arachler 1254") at about 230°. On cooling these solutions, the polymer separated. In one experiment, the polymer gave an inherent viscosity of about 0.05 dl./g. at 230° in mixed tetrachlorobiphenyl. No attempt was made to stabilize the polymer against degradation during its dissolution and subsequent viscosity determination. No molecular weight determinations were made either by osmotic or light scattering method on account of the inherent difficulties of operation at the required high temperature.

When poly(methylene sulfide) was heated in a sublimator (bath temperature 190°) white needle-like crystals were slowly deposited on the cold finger. After two crystallizations from benzene, the sublimate gave an infrared spectrum and x-ray diffraction pattern, which were identical with those obtained from an authentic sample of *s*-trithiane. Molecular weight values of 154 and 161 were obtained for the sublimate and *s*-trithiane in benzene solution by the ebullioscopic method. These values are in fair agreement with each other, but are higher than the value 138 calculated for $C_3H_6S_3$.

The decomposition behavior of poly(methylene sulfide) to produce *s*-trithiane is believed to be due to the presence of some chloromethyl end groups of the polymer molecules. Presumbaly, the formation of the trithiane takes place *via* cyclic sulfonium salt formation:



Polymer molecules, which do not contain a halomethyl end group, cannot form the sulfonium salt and thus fail to give trithiane. Wohl's[6] polymer failed to sublime, because in

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[1] Contribution No. 251 of the Goodyear Tire & Rubber Company.

[2] Sample kindly supplied by Stauffer Chemical Company.

[3] The heating rate during the melting range was 0.5° per minute or slower. The lower limit denotes the onset of liquefaction, while the upper limit represents the temperature for the complete disappearance of birefringence under the polarizing microscope.

[4] J. de Lattre, *Chem. Zentr.*, **83II**, 1192 (1912).

[5] F. Runge, Z. El-Hewehi, and D. Hempel, *J. Prakt. Chem.*, **8**, 1 (1959).

[6] A. Wohl, *Ber.*, **19**, 2344 (1886).

his method of synthesis involving hydrogen sulfide and hexamethylenetetramine no halomethyl end groups can be present. This mechanism, based on sulfonium salt formation, was invoked by Bell, *et al.*[7] to explain "two classes" of poly(ethylene sulfides), namely, Class I which does not give *s*-dithiane on heating and Class II which gives the dithiane. We also observed the formation of dithiane on heating poly(ethylene sulfide) which was prepared by the reaction of 1,2-dibromoethane and sodium sulfide in equimolar proportions.

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(7) E. V. Bell, G. M. Bennett, and A. L. Hock, *J. Chem. Soc.*, 1803 (1927).

Reduction of 3-Cholestanone with Lithium Aluminum Hydride–Aluminum Chloride

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In a previous paper from these laboratories[1b] it was shown that the reduction of 4-*t*-butylcyclohexanone with lithium aluminum hydride–aluminum chloride (1:4 ratio) in excess gives 80% of the *trans* (equatorial) 4-*t*-butylcyclohexanol, *i.e.*, less than the 89–91% *trans*-alcohol formed with lithium aluminum hydride alone.[1,2]

Compared to these results, the value of 99% 3-β-cholestanol reported by Wheeler and Mateos[3] for the reduction of 3-cholestanone with a mixture of lithium aluminum hydride–aluminum chloride seemed surprising, especially since the reduction of 3-cholestanone with lithium aluminum hydride alone is reported to give 88–91% of the (equatorial) alcohol[4] thus being very similar to the reduction of 4-*t*-butylcyclohexanone. This prompted us to restudy the reaction with the mixed hydride.

Preliminary experiments[5] indicated that in the presence of the usual excess (25–100%) of reducing agent (lithium aluminum hydride–aluminum chloride) variable amounts of unchanged 3-cholestanone were recovered. When a larger excess of hydride was used (10 equivalents of hydride per mole of ketone), the products of reduction were ketone-free and contained 18 ± 2% of 3-α-cholestanol (axial) according to the specific rotation of the acetate of the reaction product. Column chromatography of the reduction product yielded 15.3% of pure 3-α-cholestanol and suggested that the total proportion of this isomer was 17%.

The difference between these values, which are well in agreement with the published results[1] for the reduction of 4-*t*-butylcyclohexanone, and the amount of 3-α-cholestanol (less than 1%) reported earlier[3] might possibly be explained as the result of some ketone being left in the reduction product obtained in the earlier[3] investigation. It is known that in the presence of ketone, lithium aluminum hydride–aluminum chloride equilibrates a mixture of equatorial and axial alcohols (such as *trans*- and *cis*-4-*t*-butylcyclohexanol), and that at equilibrium almost the entire alcohol (99% or more) is in the form of a complex of the equatorial isomer. We were able to bring about such an equilibration by boiling the reaction product of 3-cholestanone (in excess) and lithium aluminum hydride–aluminum chloride overnight in ether solution. The only alcoholic material isolated from this reaction was 3-β-cholestanol.

The equilibration of the $R\text{-}OAlCl_2$ complex of the cholestanols (R-OH) must be distinguished (*cf.* ref. 1) from the equilibration of the free 3-cholestanols which gives 84% 3-β (equatorial) and 16% 3-α isomer,[4a] similarly to the equilibration of 4-*t*-butylcyclohexanol which gives 77–81% equatorial isomer.

EXPERIMENTAL[6]

Reduction with lithium aluminum hydride–aluminum chloride. (A) In a typical experiment, 0.88 g. (2.27 mmoles) of 3-cholestanone (m.p. 132–133°; $[\alpha]_D^{24}$ + 42.5°)[7] in 200 ml. of dry ether was added over a period of 2 hr. to the reducing agent prepared as described before[1] from 2.1 g. (15.7 mmoles) of aluminum chloride in 50 ml. of ether and 5 ml. (5.3 mmoles) of a 1.06*M* solution of lithium aluminum hydride in ether. The crude product, isolated in the usual manner, was heated for 3 hr. on a steam bath with 25 ml. of acetic anhydride and 15 ml. of dry pyridine to give 0.91 g. (95% overall yield) of crude 3-cholestanyl acetates, $[\alpha]_D^{24}$ + 16.8 ± 0.2° which corresponds to 18.0 ± 2% of the 3-α-isomer if the specific rotations are taken as +13.9°[8,9] for the 3-β isomer and +30.0°[8] for the 3-α isomer.

(1a) To whom inquiries regarding this note should be directed.

(1b) E. L. Eliel and M. N. Rerick, *J. Am. Chem. Soc.*, **82**, 1367 (1960).

(2) E. L. Eliel and R. S. Ro., *J. Am. Chem. Soc.*, **79**, 5992 (1957).

(3) O. H. Wheeler and J. L. Mateos, *Chem. & Ind.* (*London*), 395 (1957); *Can. J. Chem.*, **36**, 1431 (1958).

(4) (a) H. R. Nace and G. L. O'Connor, *J. Am. Chem. Soc.*, **73**, 5824 (1951). (b) C. W. Shoppee and G. H. R. Summers, *J. Chem. Soc.*, 686 (1950). We repeated this reduction to check our analytical method and found 91% β-cholestanol (see Experimental).

(5) E. L. Eliel, M. N. Rerick, and L. A. Pilato, unpublished observations.

(6) All melting points were taken on a Kofler block and are uncorrected. Rotations were determined in a 2-dm. tube in 2–3% chloroform solution.

(7) H. S. Anker and K. Bloch, *J. Am. Chem. Soc.*, **66**, 1752 (1944) have reported m.p. 128.8–129.8° and $[\alpha]_D$ +42.7°.