the *d-cis*-carveol derivative, m.p. 92.5°, $[\alpha]_D$ 44.2° ($CHCl_3$, *c* 2).

In a similar manner the *p*-nitrobenzoate was prepared giving a mixture melting mainly at 27–28° and completely melted at 70–72°. Recrystallization gave a mixture of transparent plates, m.p. 26–28°, and a powder, m.p. 75–78°, after mechanical separation. This compares with the report[3] of the *d-cis* derivative m.p. 26.5–28° and the *d-trans* derivative, m.p. 77°.

Boiling 10.78 g. of the carveol mixture with 10 ml. of acetic anhydride and 1.0 g. of anhydrous sodium acetate for two hours gave on distillation 9.56 g. of carveol acetate, b.p. 110–113° (12 mm.), n^{20}_D 1.4760, α_D −33.2°.

Oxidation of 6.0 g. of the carveol mixture in 12.5 ml. of glacial acetic acid with 5.4 g. of chromic anhydride in 12.5 ml. of acetic anhydride at 13–17° gave carvone, α_D −54.6°, n^{20}_D 1.4959. This indicates that little isomerization of the ring structure occurred during the reduction and subsequent oxidation.[4,5]

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(4) This reaction was carried out by Mr. V. J. Baarman.

(5) Unless otherwise indicated all notations taken on homogeneous materials.

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The Vapor Pressures of Some Substituted Benzotrifluorides[1]

BY SAMUEL KARDON AND JOHN H. SAYLOR

RECEIVED JANUARY 16, 1953

The measurements reported in this note resulted from a continuation of a general program in this Laboratory concerning the solubility and other physical properties of organic fluorine compounds.

TABLE I

PHYSICAL CONSTANTS AND CONSTANTS OF THE VAPOR PRESSURE EQUATION

Benzotrifluoride	B.p., °C. Calcd.	F.p., °C. Obsd.	Dep.	$\eta^{20°}D$	$\eta^{30°}D$	$\epsilon^{30°}$	*A*	*B*	*C*
m-Nitro	202.75	−1.32	0.06	1.4719	1.4675	17	7.18025	1710.60	195.12
m-Amino	191.13	5.65	.01	1.4788	1.4750		7.17030	1650.21	193.58
3-Nitro-4-chloro	222.58	−2.54	.04	1.4895	1.4853	12.8	7.15778	1738.71	183.95
2-Chloro-5-nitro	231.88	21.7	.5		1.5043	9.8	7.15409	1779.91	184.64

Experimental

Materials.—The compounds were supplied by the Hooker Electrochemical Company and were further purified by distillation at reduced pressure (controlled to ±0.1 mm.) in a silvered vacuum-jacketed glass column packed with 1/8" glass helices. The fractions used were characterized by measuring refractive indices, dielectric constants and freezing points. The dielectric constants were measured by the heterodyne beat method. The apparatus was calibrated with benzene and chlorobenzene and has been found to give good results in measuring dielectric constants of highly purified materials with values up to approximately 15. The freezing points were determined as previously described.[2]

Vapor Pressures.—The apparatus which was previously used by Potter[2] was employed. It was a modification of the boiling point apparatus described by Rossini and coworkers.[3]

Results

Fifteen to twenty individual measurements were made on each compound from approximately 5 to 740 mm. The data were fitted by the method of least squares to the equation

$$\log p = \frac{-B}{t + C} + A$$

where *p* is the pressure in mm. and *t* is the temperature in degrees centigrade.

The standard deviation between the observed pressures and those calculated from the equation ranged from 0.09 to 0.11 mm.

Table I gives the boiling points calculated from the vapor pressure equation, the freezing points, the freezing point depressions, the refractive indices (η), the dielectric constants (ϵ) and the values of the three constants in the above equation. The value given for the dielectric constant of *m*-nitrobenzotrifluoride is not considered as reliable as those for the other compounds.

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(1) Part of the work reported was carried out under Contract N6ori-107, T. O. II with the Office of Naval Research. Taken from the thesis submitted by Samuel Kardon to the Graduate School of Duke University in partial fulfillment of the requirements for the degree of Master of Arts, June 1952.

(2) J. C. Potter and J. H. Saylor, THIS JOURNAL, **73**, 90 (1951).

(3) C. B. Willingham, W. J. Taylor, J. M. Pignocco and F. D. Rossini, *J. Research Natl. Bur. Standards*, **35**, 219 (1945).

Polyalkylene Sulfides. XII.[1] Termination by Disulfide Formation[2]

BY C. S. MARVEL, C. W. HINMAN AND H. K. INSKIP

RECEIVED DECEMBER 18, 1952

It has been observed[3] that 96–98% of the thiol groups have reacted in 8 to 16 minutes when hexamethylenedithiol and biallyl polymerize in a persulfate initiated reaction at 30°. The complete disappearance of thiol groups occurs only after many hours. The polymer formed in the first few minutes has an inherent viscosity of 0.4 to 0.7 and that obtained after a much longer reaction time has an inherent viscosity of about 1.0. Other dithiols and diolefins show a similar behavior. This has suggested to us that the slow reaction may be an oxidation of terminal thiol groups in the polymers first formed, to yield a disulfide which thus terminates further polymerization.

Evidence of the presence of disulfide links in the polymers of higher inherent viscosity produced in the above reaction has now been obtained. If one of the polymers produced in the long reaction time is reduced by amalgamated zinc and hydrochloric acid in hot xylene solution, it is cleaved to a polymer of lower inherent viscosity. This reduction product can be reoxidized with iodine to produce a poly-

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(1) For the eleventh communication on this topic, see C. S. Marvel and H. N. Cripps, *J. Polymer Sci.*, **9**, 53 (1952).

(2) The work discussed herein was performed as a part of the research project sponsored by the Reconstruction Finance Corporation, Office of Synthetic Rubber, in connection with the Government Synthetic Rubber Program.

(3) C. S. Marvel and A. H. Markhart, Jr., THIS JOURNAL, **73**, 1064 (1951).

mer of approximately the same inherent viscosity as that before the reduction.

A polymer which is produced in the first rapid reaction between hexamethylenedithiol and biallyl (inherent viscosity 0.472) has been isolated and oxidized with iodine to produce a product with a higher viscosity which resembles in all ways a product formed by the usual long polymerization process. Moreover, this polymer can be again reduced to give a product of lower inherent viscosity.

It is a significant fact that reduction of the higher molecular weight product does not reduce the viscosity enough to indicate that all material present after reduction is half of the original molecular weight. Neither does oxidation of a low viscosity polymer double the molecular weight, as a rule. This would suggest that not all the high molecular weight polyalkylene sulfide molecules contain a central disulfide linkage. Some termination of the polymerization reaction may involve dimerization of carbon free radical intermediates as was suggested earlier.[3]

Polyhexamethylene sulfides were also prepared from hexamethylenedithiol and biallyl with azo-bis-isobutyronitrile as the initiator. In 18 hours at 50° these polymers grew to an inherent viscosity of 0.5 to 0.65. These polymers could be oxidized with iodine to give polymers with an inherent viscosity of over 1.0. The unoxidized polymers were not reduced in viscosity when treated with zinc and acid in xylene solution. Hence they apparently still retain the mercaptan end groups.

Experimental

All inherent viscosities were determined on solutions of 0.20 g. of polymer in 50 ml. of chloroform at 25°.

Preparation of Polymers.—Polyhexamethylene sulfide polymers (inherent viscosity of 0.8 to 0.9) were prepared as described earlier[4] and also by initiating the reaction with azo-bis-isobutyronitrile. This initiator was used in the standard acetate buffered emulsions at *p*H 3.5 and the mixture tumbled at 50° for 18 hours. The ammonium persulfate, sodium bisulfite, cupric sulfate and *p*-*t*-butylcatechol used in the standard method were omitted and 0.03 g. of azo-bis-isobutyronitrile was introduced. The polymers were isolated as before. Polymers were obtained in 94–99% yield which had inherent viscosities of 0.5 to 0.65.

Reduction of High Molecular Weight Polyhexamethylene Sulfide Polymers.—One gram of persulfate initiated polymer (inherent viscosity 0.829) was dissolved in 150 ml. of xylene. Amalgamated zinc (about 30 g.) was added, stirring was started, the temperature was raised to 80° and then over a period of 12 to 18 hours 30 ml. of aqueous hydrochloric acid (one part of sp. gr. 1.19 hydrochloric acid to one part of water) was added at the rate of three to five drops per minute. After that time the mixture was cooled, filtered and poured into a large excess of cold methanol. The polymer isolated had an inherent viscosity of 0.537. Analytically its composition was unchanged. The melting point and appearance of the polymer was also essentially unchanged.

Oxidation of Low Molecular Weight Polyhexamethylene Sulfide Polymers.—One gram of persulfate initiated polymer (produced in the first five to eight minutes of reaction, inherent viscosity 0.472) was dissolved in 50 ml. of chloroform and to the solution was added about 0.2 g. of iodine. The solution was tumbled at 50° for about 24 hours, much of the solvent evaporated and the polymer isolated by pouring the residue into methanol. The product isolated had an inherent viscosity of 1.013 and in all respects appeared to be identical with a polymer produced in the usual long time polymerization.

Other Oxidation and Reduction Experiments.—In the following tables are collected the results of a number of oxidation and reduction experiments on a variety of polyhexamethylene sulfides.

TABLE I

REDUCTION AND REOXIDATION OF PERSULFATE INITIATED POLYHEXAMETHYLENE SULFIDES

Experiment no.	Inherent viscosity Of original polymer	After zinc reduction	After reoxidation with I_2
3–4[a]	0.691	0.514	. . .
7–5	.801	.633	0.815
7–4	.829	.537	0.780
6•2	.921	.849	1.039

[a] The polymer used in experiment 3–4 had the following analysis: C, 62.31; H, 10.26; S, 27.67. After reduction with zinc the analysis was: C, 61.89; H, 10.13; S, 27.22. The calculated values of $[C_6H_{12}S]_x$ are C, 62.00; H, 10.41; S, 27.59.

TABLE II

AZO-BIS-ISOBUTYRONITRILE INITIATED POLYHEXAMETHYLENE SULFIDES

Experiment no.	Original inherent viscosity	Inherent viscosity After oxidation with I_2	After subsequent reduction
12–9	0.617	. . .	0.605[a]
6–6	.657	0.812	.664
12–7	.507	1.295	.703
12–8	.507	1.194	. . . .
6–7	.478	0.650	. . . .

[a] This sample was reduced without intermediate oxidation.

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[4] C. S. Marvel and G. Nowlin, THIS JOURNAL, 72, 5026 (1950).

Some Xanthineacetic Acid Derivatives

BY FREEMAN H. MCMILLAN AND H. M. WUEST

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In continuation of our program in the search for new analeptic drugs[1] it was decided to prepare N,N-diethyltheophylline-7-acetamide and N,N-diethyltheobromine-1-acetamide. The preparation of these and some closely related compounds together with some observations concerning their chemical properties constitute the subject matter of this paper.

Theophylline-7-acetic acid was prepared as described in the literature.[2] This acid was converted by usual methods to the ethyl ester in 83% yield and to the acid chloride in 36% yield. Theophylline-7-acetamide was prepared by shaking a benzene solution of theophylline-7-acetyl chloride with ice and excess ammonium hydroxide. N,N-Diethyltheophylline-7-acetamide was not obtained by treatment of theophylline-7-acetyl chloride with excess diethylamine in benzene; this was prepared, however, by treatment of theophylline with N,N-diethylchloroacetamide in aqueous sodium hydroxide solution or, in better yield, in ethanolic sodium hydroxide solution.

As in the case of 2-(3-pyridazonyl)-acetic acid,[3] theophylline-7-acetic acid when refluxed with acetic anhydride and pyridine, gave off carbon dioxide

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[1] For the previous paper on this topic see F. H. McMillan and J. A. King, THIS JOURNAL, 73, 3165 (1951).

[2] E. Merck, O. Wolfes and E. Kornick, German Patent 352,980, March 20, 1922.

[3] J. A. King and F. H. McMillan, THIS JOURNAL, 74, 3222 (1952).