a magnetic field (Verdet constant), it was considered of interest to measure the Verdet constant to note if it, too, was unusual. Indeed, such was found to be the case.

The eight fluorocarbons studied are listed in Table I along with the measured values of their Verdet constants at 25° and for 5893 Å. It will be noted that the Verdet constants for these fluorinated hydrocarbons are extraordinarily low. The lowest value, that belonging to hexadecafluoroheptane, is about one-half the lowest previous value listed for any compound in the "International Critical Tables."

TABLE I

VERDET CONSTANTS OF SOME LIQUID FLUOROCARBONS AT 25° AND FOR 5893 Å[a]

Compound	Molecular weight	Density, 25°, g./cc.	Verdet constant, min./gauss-cm.
Hexadecafluoroheptane	388	1.7208	0.003500
(Trifluoromethyl)undecafluorocyclohexane	350	1.7871	.003751
bis-(Trifluoromethyl)-decafluorocyclohexane	400	1.8391	.003950
bis-(Trifluoromethyl)-chlorononofluorocyclohexane	416	1.8711	.005252
Chlorotrifluoroethylene polymer	713	1.9412	.009093
Chlorotrifluoroethylene polymer	866	1.9681	.009118
Chlorotrifluoroethylene polymer	911	1.9736	.009168
Fluorolube oil	860	2.0081	.004739

[a] The values of molecular weight and density found in this table were supplied by the Carbide and Carbon Chemicals Corporation, Oak Ridge, Tennessee.

Enough data are present in Table I to enable a calculation to be made of the molecular magnetic rotation[2] (utilizing MV/d for water at 25° and 5893 Å. as 0.2353). From this, values of the increment attributable to the fluorine atom may be made. For the cases presented here, the values vary, no doubt due to constitutive factors.

Acknowledgments.—It is a pleasure to acknowledge our indebtedness to Dr. Clifford Beck of the Carbide and Carbon Chemicals Corporation, Oak Ridge, Tennessee, for the loan of the compounds studied and for data concerning them. The author is also indebted to the Department of Physics of Columbia University, particularly to Dr. Lucy Hayner, for permission to use the Faraday Effect equipment.

Experimental

The measurements of the Verdet constant were made on the Faraday Effect apparatus of the Department of Physics, Columbia University. The procedures used were the same as those described by Slack[3] and the author[2] and will not be repeated here. The fluorocarbons were obtained through the courtesy of the Carbide and Carbon Chemicals Corporation, Oak Ridge, Tennessee, where they had been subjected to fractional distillation and their molecular weight and density measured.

EMORY UNIVERSITY
EMORY UNIVERSITY, GEORGIA

RECEIVED SEPTEMBER 29, 1948

A Synthesis of Symmetric Phosphinic Acids

BY GENNADY M. KOSOLAPOFF

Michaelis and Wegner[1] were the first to employ the Grignard reaction in the synthesis of aromatic phosphinic acids under conditions which precluded the formation of by-products, by the reaction of aryl magnesium halides with N-piperidyl dichlorophosphate. Their lone paper on this subject, however, failed to state the yields obtained, although these were said to have been "good." Because of the relatively high cost of piperidine, it was thought that an equally good reagent might be found among the more available aliphatic dialkyl amines, which can be readily converted to the corresponding dichlorophosphates. This belief has been realized and excellent yields of some symmetric aromatic and aliphatic phosphinic acids have been readily attained by using N,N-diethylamine to block one reactive group of phosphorus oxychloride. The reaction, thus, may be extended to the aliphatic series, which has not been done previously.

Experimental

The yields and the properties of the products are given in the table.

SYMMETRIC PHOSPHINIC ACIDS PREPARED

Derivative	Yield, %	M. p., °C.	Equiv. weight Calcd.	Equiv. weight Found
bis-*p*-tolyl	75	131–132	......	....[1]
bis-*p*-anisyl	79	179–180	278	275
bis-*o*-anisyl	74	227–228	11.15%[a]	11.1%[a]
Di-*n*-butyl	82	70.5–71	178	176

[a] % Phosphorus.

bis-*p*-Tolylphosphinic Acid.—N,N-Diethylamidodichlorophosphate (19 g., 0.1 mole) was added during one hour to a gently refluxing solution of *p*-tolylmagnesium bromide, prepared from 34.2 g. of *p*-bromotoluene and 4.8 g. of magnesium, in 300 ml. of dry ether. After refluxing for two hours, the mixture was hydrolyzed by means of ice-water and ammonium chloride, and the organic layer was treated with 250 ml. of concentrated hydrochloric acid. Ether was distilled from the mixture and the residue was refluxed for four hours. After cooling, the product was filtered and was recrystallized from dilute ethanol It formed long colorless needles. Michaelis and Wegner[1] reported its m. p. 130–132°.

bis-*p*-Anisylphosphinic Acid.—The same procedure, using 37.4 g. of *p*-bromoanisole for the Grignard reagent, yielded this acid in the form of short colorless needles.

bis-*o*-Anisylphosphinic Acid.—The same procedure using *o*-bromoanisole gave this substance, in the form of needles; this preparation was also checked by synthesizing the product from phosphorus oxychloride and the Grignard reagent by an earlier procedure.[2] The rather unexpectedly high melting point, in comparison with the *p*-isomer, may be caused by interaction of the oxygen atom of the *o*-methoxyl group, with the PO_2H group.

Di-*n*-butylphosphinic Acid.—A procedure similar to the above was used with 57 g. of the dichlorophosphate and the Grignard reagent from 82.2 g. of *n*-butyl bromide and 14.58 g. of magnesium; the addition period was two hours and the reflux period was three hours. After hydrolysis by refluxing with hydrochloric acid, the bulk of the latter was distilled, the residue made strongly alkaline with sodium hydroxide, and the regenerated

---

[2] R. T. Lagemann, *J. Polymer Sci.*, **3**, 663 (1948).

[3] F. G. Slack, *Phys. Rev.*, **46**, 945 (1934).

[1] Michaelis and Wegner, *Ber.*, **48**, 316 (1915).

[2] Kosolapoff, THIS JOURNAL, **64**, 2982 (1942).

amine was steam distilled. The crude product m. p. 66–69°, was isolated by ether extraction and converted to the corresponding chloride (for separation from possible traces of butanephosphonic acid) by warming with 51.5 g. of phosphorus pentachloride followed by distillation; b. p. 156–157° at 28 mm. Hydrolysis of the chloride with warm water and crystallization from hexane gave the pure acid in the form of long silky colorless needles. This acid was previously reported by Plets[3] who prepared it by hydrolysis of either R_2PCl_3 or R_2POCl, which were, in turn, derived from dibutylchlorophosphine; he gave m. p. 31–32° for the acid. The higher melting point of the present preparation indicates either higher purity or, possibly, an isomeric form.

---

[3] Plets, dissertation, Kazan, U. S. S. R., 1938.

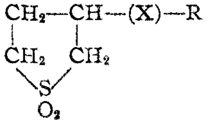
THE ROSS CHEMICAL LABORATORY
ALABAMA POLYTECHNIC INSTITUTE
AUBURN, ALABAMA

RECEIVED SEPTEMBER 21, 1948

Preparation and Properties of Tetramethylene Sulfones

BY MARLIN T. LEFFLER AND W. D. KRUEGER

In the course of a search for new types of chemotherapeutic agents, several cyclotetramethylene sulfones were prepared and studied. These were synthesized by the addition of amines, alcohols and mercaptans to 2,5-dihydrothiophene-1-dioxide (butadiene sulfone) in a manner similar to that described by Delfs.[1] The general formula, I, illus-

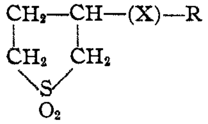


(I)

trates the types prepared and listed in Table I, where (X) is either –NH–, –O– or –S–, and R is an alkyl or substituted alkyl group.

TABLE I

CYCLOTETRAMETHYLENE SULFONES,



(X)—R	M. p., °C.	Yield, %	Formula	Analyses, N, % Calcd.	Analyses, N, % Found
		Amine Hydrochlorides			
$-NHC_4H_9\text{-}n\cdot HCl$	148–149	73 (base)	$C_8H_{18}ClNO_2S$	6.15	6.14
$-NHCH_2CH_2C_6H_5\cdot HCl$	188–189	41	$C_{12}H_{18}ClNO_2S$	5.08	5.00
$-NH(CH_2)_3N(C_2H_5)_2\cdot 2HCl$	176–177[a]	77	$C_{11}H_{26}Cl_2N_2O_2S$	8.72	8.49
$-NC_5H_{10}$(Piperidino)$\cdot HCl$	218–219	76 (base)	$C_9H_{18}ClNO_2S$	5.84	5.86
		Ethers			
$-O(CH_2)_2N(C_2H_5)_2$	Phosphate: 132–133 Base: B. p. 175–181 (4 mm.)	62	$C_{10}H_{24}NO_7PS$	4.20	4.31
$-SCH_2C_6H_5$	61–63	51	$C_{11}H_{14}O_2S_2$	C: 54.52 H: 5.82	54.48 5.53
$-S(CH_2)_2N(C_2H_5)_2$	HBr: 122–123	48	$C_{10}H_{22}BrNO_2S_2$	4.22	4.27

[a] Dihydrochloride precipitated by addition of excess alcoholic hydrogen chloride to an acetone solution of the base. Recrystallized from absolute alcohol.

It is of interest to note that while the addition of amines to butadiene sulfone does not generally require a catalyst, alcohols and mercaptans react best in the presence of an alkaline agent. Triton-B was found to be an effective catalyst; sodium and potassium hydroxides serve also. Worth emphasizing is the fact that strongly basic amines such as aliphatic amines, phenethylamine, etc., add readily to the double bond of butadiene sulfone but less basic amines, aniline and benzylamine for example, do not react to give any appreciable yield under similar conditions.

Through the courtesy of the Division of Chemotherapy for Tropical Diseases, National Research Council, the products described herein were tested for activity against a variety of tropical diseases. None was found to have any significant activity in amebiasis, filariasis, schistosomiasis or leischmaniasis.

We are indebted to Mr. E. F. Shelberg of the Microanalytical Department for the microchemical analyses.

Experimental

The sample of 2,5-dihydrothiophene-1-dioxide (butadiene sulfone) used in this work was furnished by the Shell Development Company under the trade name "Sulfolene."

The tetrahydrothiophene-1-dioxides listed in Table I were prepared by the following general procedures:

3-Amino Derivatives.—A mixture of 0.5 mole of butadiene sulfone and 2 moles of the primary or secondary amine was stirred and heated at 70–80° for twenty-four hours. The excess amine was then removed by distillation *in vacuo* and the residue was dissolved in 300 ml. of anhydrous ether, which solution was treated with excess dry, gaseous hydrogen chloride to form the salt. The solid salts were removed by filtration and recrystallized to constant melting point from absolute alcohol.

3-Substituted Ethers.—A mixture of 0.5 mole of butadiene sulfone, 1.0 mole of the desired alcohol and 2 to 4 ml. of Triton-B was heated at 70–80° for twenty-four hours. At the end of this time the Triton-B was neutralized with concentrated sulfuric acid and the excess of the alcohol used was removed by distillation *in vacuo*. The residue was then distilled under reduced pressure. In the case of the 3-diethylaminoethoxy derivative, the product was converted to the phosphate by the addition of a slight excess of phosphoric acid (85%) to an alcoholic solution of

---

[1] Delfs, U. S. Patent 2,219,006 (1940); 2,291,798 (1942).