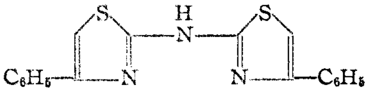
TABLE I

Compound	Formula	Yield, %	M. p., °C. Found[c]	M. p., °C. Reported	Composition,[h] % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
2-Amino-4-phenylthiazole	$C_9H_8N_2S$	67[a]	151–152	151–152[d]	...	...	..	..
Acetyl derivative	$C_{11}H_{10}ON_2S$		213–214	214.5–215[d]	...	...	..	..
2,4-Diphenylthiazole	$C_{15}H_{11}N_2S$	84[a]	91–92	92–93[e]	[i]	[i]	..	..
2-Amino-4-hydroxythiazole	$C_3H_4ON_2S$	34[a]	233–238, dec.	[f]	31.03	30.81	3.45	3.53
bis-(4-Phenyl-2-thiazolyl)-amine	$C_{18}H_{13}N_3S_2$	40, 78[b]	218–220	[g]	64.55	64.35	3.89	4.11
Acetyl derivative	$C_{20}H_{15}ON_3S_2$		132–133	[g]	63.16	63.45	4.25	4.14

[a] Based on the diazoketone. [b] The same compound was obtained with one or two molecular portions of diazoacetophenone, the latter giving the 78% yield, based on the dithiobiuret. [c] All melting points observed on a Fisher–Johns melting point block. [d] These compounds were compared with authentic material previously prepared in this Laboratory, reference 1.[a] [e] Hubacher, *Ann.*, **259**, 237 (1890). [f] Andreasch, *Monatsh.*, 8, 424 (1887), reported a melting point of 208° (dec.) for this material prepared by a different method. The compound from the diazoketone reaction melted in this range above. Similar results were obtained by Allen and VanAllan, "Organic Syntheses," **27**, 71 (1947). [g] Not previously reported. [h] Analysis by Miss P. Craig. [i] Calcd.: N, 5.62. Found: N, 5.69.

2-amino-4-hydroxythiazole (pseudothiohydantoin). Thiourea and thiobenzamide yield with diazoacetophenone, 2-amino-4-phenylthiazole and 2,4-diphenylthiazole, respectively. With the same diazoketone dithiobiuret gives bis-(4-phenyl-2-thiazolyl)-amine (I).[4]



I

Evidence for the structure of I lies in the method of formation, the analysis of the compound and its N-acetyl derivative, and the fact that it was unaffected by both acid and alkaline hydrolytic conditions, contrary to the known sensitivity of the thioureido group.[5] Compound I was also prepared by the action of phenacyl bromide on dithiobiuret.

Data for the compounds prepared are listed in Table I.

This investigation was supported by a grant from the Abbott Fund of Northwestern University.

Experimental

Preparation of Materials.—Diazoacetophenone was prepared as previously described.[3] Ethyl diazoacetate was prepared by the method of Curtius.[6] Thiobenzamide was prepared by suspending 60.5 g. (0.5 mole) of benzamide and 22.2 g. (0.10 mole) of phosphorus pentasulfide in 300 cc. of benzene and refluxing until the benzamide dissolved. The hot benzene solution was filtered and cooled, and the thiobenzamide collected. The material was recrystallized once from benzene m.p. 115–116°.[7] The dithiobiuret was a commercial sample, obtained through the courtesy of the American Cyanamid Company.

Preparation of the Thiazoles.—The techniques used will be illustrated by the following examples.

(a) **2-Amino-4-phenylthiazole.**—A solution of 1.46 g. (0.01 mole) of diazoacetophenone and 2.40 g. (0.012 mole) of thiourea in 20 cc. of absolute alcohol was refluxed for one hour. A portion of the alcohol was evaporated, a small amount of water and charcoal added, and the hot solution filtered and cooled. The separated material was collected and recrystallized from dilute aqueous alcohol.

(b) **bis-(4-Phenyl-2-thiazolyl)-amine.**—A solution of 2.92 g. (0.02 mole) of diazoacetophenone and 1.48 g. (0.011 mole) of dithiobiuret was refluxed for one hour in alcoholic solution. The product separated from the solution, was filtered and dissolved in excess acetone. Dilute aqueous alcohol was added and the acetone removed carefully on the steam-bath. The material crystallized on cooling and was recrystallized in the same manner.

bis-(4-Phenyl-2-thiazolyl)-amine was also prepared by refluxing 4.0 g. (0.02 mole) of phenacyl bromide and 1.50 g. (0.01 mole) of dithiobiuret in 25 cc. of alcohol for one hour. The separated material was suspended in alcohol and digested with ammonium hydroxide for one-half hour, filtered and washed with a small amount of alcohol. Recrystallization gave a material identical with that prepared above.

Acetyl Derivatives of Thiazoles.—These were prepared by the action of acetic anhydride on approximately 0.3 g. of the amino thiazole. The products were recrystallized from dilute aqueous alcohol.

Attempted Hydrolysis of I.—A solution of 0.1 g. of the material in 30 cc. of hot alcohol and 10 cc. of water was heated under reflux for three hours with 10 g. of barium hydroxide. Only the starting material was recovered, m.p. 217–218°.

Attempted acid hydrolysis performed in the same manner yielded identical results.

DEPARTMENT OF CHEMISTRY
NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS

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The Verdet Constant of Certain Liquid Fluorocarbons

BY R. T. LAGEMANN

It is now known that certain fluorinated hydrocarbons possess some unusual physical properties. Although the density and viscosity are not particularly different from those of other liquids, the refractive index and ultrasonic velocity are both extraordinarily low. As an example, consider bis-(trifluoromethyl)-chlorononofluorocyclohexane. Here $n^{60}{}_D$ is 1.3021,[1] only three liquids in Lange's "Handbook" have a lower value, and the ultrasonic velocity at 20° is 691.8 m./sec.,[1] also extremely low relative to other liquids. Since no values are known for the rotation of the plane of polarization of light by these liquids when placed in

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[4] The descriptive literature of the American Cyanamid Company records the reaction of chloroacetone and dithiobiuret to produce 2-thioureido-4-methylthiazole. Attempts to obtain the analogous 2-thioureido-4-phenylthiazole were not successful.

[5] Mehta and Krall, *J. Indian Chem. Soc.*, **12**, 635 (1935), report the effects of acid and basic hydrolysis of phenylthiourea.

[6] Curtius, *J. prakt. Chem.*, **38**, 401 (1888).

[7] Gabriel and Heyman, *Ber.*, **23**, 158 (1890).

[1] Lagemann, Woolf, Evans and Underwood, THIS JOURNAL, **70**, 2994 (1948).

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

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

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

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

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

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