upon mixing with a moist ether solution of picric acid gave only imidazole picrate. In contrast with these properties the ketone (II) was resistant to hydrolysis by 0.5 *N* sodium hydroxide at reflux temperature and gave a picrate derivative, m.p. 204°.[1]

Attempts to acetylate benzimidazole, 2-methylbenzimidazole and lophine (2,4,5-triphenylimidazole) using isopropenyl acetate were unsuccessful.

Experimental[3]

1-Acetylimidazole (I).—A mixture of 2.0 g. (0.03 mole) of imidazole, m.p. 89–90°, and 20 ml. of isopropenyl acetate containing 10 drops of concentrated sulfuric acid in a 50-ml. round-bottomed flask equipped with a six-bulb Snyder column with condenser attached was heated sufficiently to keep the gas temperature at the top of the column at 60° for one hour. During this time acetone with traces of isopropenyl acetate was collected from the condenser. The reaction mixture was treated with anhydrous sodium carbonate to neutralize the sulfuric acid. The liquid portion was decanted from the solid and evaporated to dryness in a dry air stream at room temperature. A residue of colorless solid product remained, wt. 3.10 g. (94% yield), m.p. 93–96°. After three recrystallizations from isopropenyl acetate, analytically pure N-acetylimidazole was obtained with a constant m.p. 101.5–102.5° (bath preheated to 96°).

Anal. Calcd. for $C_5H_6ON_2$: C, 54.53; H, 5.49; N, 25.45. Found: C, 54.45; H, 5.38; N, 25.25.

The preparation of a picrate derivative which was attempted in moist ether gave a compound identical with the picrate of imidazole, m.p. and mixed m.p. 212.5–213.5°.[4]

Anal. Calcd. for $C_9H_7O_7N_5$: C, 36.37; H, 2.37; N, 23.57. Found: C, 36.53; H, 2.34; N, 23.50.

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(3) Microanalyses by Mr. Goji Kodama, Chemistry Department, University of Michigan.

(4) Oddo and Ingraffia[1] report a m.p. 212° but no analytical data. R. G. Fargher and F. L. Pyman, *J. Chem. Soc.*, **115**, 217 (1919), report a m.p. 212° and a nitrogen content of 23.3%.

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Densities of Mixtures. Water and Methanol

BY G. CHAPAS

RECEIVED AUGUST 25, 1952

Writing on the densities of mixtures: water + methanol, Clifford and Campbell stated that *no simple equation (of third degree or less) can represent the results of their determinations.*[1] However computation of the specific volumes or, better, of the molal volume *V* of these mixtures shows that additivity is almost satisfied on the whole scale of composition; more precisely the volume of a mixture is very nearly equal to the sum of the volumes of its constituents, the deviation being not larger than 3% for about $N = 0.5$.

The mean molal volumes calculated from the authors' data are given in the second column of Table I for each value of the mole fraction *N* of methanol.

By application of the method of least squares, we get the equation

$$V = 18.088_6 + 18.676_5\,N + 3.988\,N^2 \qquad \text{(A)}$$

The coefficient of the third degree term would be very small and it is preferable to neglect it.

The values of *V* drawn from this equation are written in the third column of the table.

TABLE I

Mole fraction, *N*	Molal volume *V*, ml. From authors' data	From equation (A)
0.000 00	18.069	18.069
.049 98	19.056	19.012
.137 79	20.693	20.718
.238 20	22.742	22.744
.375 28	25.624	25.639
.519 84	28.843	28.855
.589 01	30.448	30.453
.789 02	35.301	35.288
.866 74	37.266	37.252
1.000 00	40.721	40.721

We may also draw from equation (A) the expressions of the partial molal volumes[2]

$$\text{Methanol}\quad V_2 = V + (1 - N)\frac{\mathrm{d}V}{\mathrm{d}N} = 36.745_1 + 7.976\,N - 3.988\,N^2$$

$$\text{Water}\quad V_1 = V - N\frac{\mathrm{d}V}{\mathrm{d}N} = 18.068_6 - 3.988\,N^2$$

or by setting $N = N_2$, $1 - N = N_1$

$$V_1 = 14.081 + 7.976\,N_1 - 3.988\,N_1^2$$
$$V_2 = 36.745 + 7.976\,N_2 - 3.988\,N_2^2$$

Then the partial molal volume V_1 of water is always decreasing and gets the minimum value for $N_1 = 0$, $V_1^0 = 14.081$ ml. in almost pure methanol; again methanol finds its minimum partial molal volume for $N_2 = 0$, that is, in pure water, $V_2^0 = 36.745$ ml.

It is not surprising that no simple equation can represent the densities of the mixtures since the molal volumes are very near to being additive; then the densities must be hyperbolic functions of the mole fraction *N* so that computation of a linear, or parabolic, or higher degree equation is without object. Emphasis must be put on the role played by the molal volume in physical chemistry and we must regret to read many interesting communications in which synthesized compounds are characterized only by melting point, boiling point or refractive index, density being lacking or given without a fairly good approximation. We might rather hope that such a constant be measured at several temperatures and the corresponding molal volumes calculated.

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(1) G. Clifford and J. A. Campbell, THIS JOURNAL, **73**, 5449 (1951).

(2) G. N. Lewis and M. Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1923.

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Chlorophenylsilanes

BY CHARLES A. BURKHARD

RECEIVED SEPTEMBER 4, 1952

Organopolysiloxane oils which contain chlorophenyl groups have been prepared and their lubricating properties studied. The preparation of these chlorophenyl-group-containing organopolysiloxane oils required that several new silanes be prepared and characterized: methyl-*p*-chlorophenyldichlorosilane, methylbis-*p*-chlorophenylchlorosilane and methyl-*m*-chlorophenyldichlorosilane. 1,3,5-Tris-*p*-chlorophenyl-1,3,5-trimethyl-

TABLE I

RESULTS OF WEAR MEASUREMENTS USING THE SHELL FOUR BALL WEAR TESTER

	Steel on					
	Steel			Brass		
Oil Load	5 kg.	10 kg.	20 kg.	5 kg.	10 kg.	20 kg.
Room temperature, 1 hour at 600 r.p.m.						
Methylsilicone	0.35 mm.[a]	0.49 mm.	..	0.59 mm.	2.33 mm.	..
Methyl-*p*-chlorophenylsilicone	.21	.33	..	.42	0.60	..
Methyl-*m*-chlorophenylsilicone	..	.35	0.53	..	.39	0.60
Room Temperature, 1 hour at 1200 r.p.m.						
Methyl-*m*-chlorophenylsilicone	..	0.41	0.49	..	0.42	0.59

[a] Average diameter of wear scar, in mm., on the three stationary balls in the Shell Four Ball Wear Tester.

cyclotrisiloxane was isolated from the hydrolysis product of methyl-*p*-chlorophenyldichlorosilane.

The chlorophenyl-containing organopolysiloxanes were prepared by the reaction of hexamethyldisiloxane and methylchlorophenylpolysiloxanes in the presence of sulfuric acid.[1] It was of interest to note that only negligible cleavage of the chlorophenyl-to-silicon bond occurred during the equilibration reaction whereas extensive cleavage of the phenyl-to-silicon bond occurs under similar conditions in phenylsiloxanes.[2]

It has been found that when these chlorophenyl-containing organopolysiloxane oils are used as lubricants they reduce the wear of steel and brass bearings over that obtained by use of the conventional methylsilicone oils. The oils were evaluated on the Shell Four Ball Wear Tester and the results of these tests are given in Table I.

Experimental

Methyl-*p*-chlorophenyldichlorosilane.—Three moles (574.5 g.) of *p*-chlorobromobenzene and 72 g. (3 moles) of magnesium turnings were allowed to react in 1.5 l. of anhydrous ether. After the reaction had proceeded to completion the ether solution of *p*-chlorophenylmagnesium bromide was added slowly with stirring to 470 g. of methyltrichlorosilane in 1 l. of anhydrous ether. After complete reaction had been effected the ether was stripped from the reaction flask and chlorosilanes were recovered by a very rapid vacuum distillation. By use of an efficient rectification column 197.2 g. of methyl-*p*-chlorophenyldichlorosilane, b.p. 161–164° (99–100 mm.), was recovered (34% yield).

Anal. Calcd. for $C_7H_7SiCl_3$: Cl (hydrolyzable), 31.44. Found: Cl (hydrolyzable), 30.9.

Methylbis-*p*-chlorophenylchlorosilane.—The low yield of methyl-*p*-chlorophenyldichlorosilane is due in part to the formation of methylbis-*p*-chlorophenylchlorosilane. In a second preparation of methyl-*p*-chlorophenyldichlorosilane 9 moles of *p*-chlorobromobenzene was used. From this run it was possible to separate cleanly methylbis-*p*-chlorophenylchlorosilane from the high boiling residue, b.p. 187° (5 mm.).

Anal. Calcd. for $C_{13}H_{11}SiCl_3$: Cl (hydrolyzable), 11.20; Cl (total), 33.59. Found: Cl (hydrolyzable), 11.5, 11.5; Cl (total), 34.5, 34.0, 33.6, 33.3, 33.1.

Methyl-*m*-chlorophenyldichlorosilane.—To a mixture of 144 g. of magnesium turnings in 3 l. of anhydrous ether was added dropwise 1000 g. of *m*-bromochlorobenzene. When the reaction had run to completion the solution of the Grignard reagent was added dropwise with stirring, to a solution of 1000 g. of methyltrichlorosilane in 500 ml. of anhydrous ether. Distillation of the reaction product gave 490.6 g. (yield 41.6%) of methyl-*m*-chlorophenyldichlorosilane, b.p. 150° (61 mm.).

Anal. Calcd. for $C_7H_7SiCl_3$: Cl (hydrolyzable), 31.44; Cl (total), 47.16. Found: Cl (hydrolyzable), 31.2; Cl (total), 47.0.

Equilibrated Methyl-*p*-chlorophenylsilicone Oil.—A solution of 160 g. of methyl-*p*-chlorophenyldichlorosilane in 150 ml. of ether was added to a vigorously stirred mixture of water and ether. After the hydrolysis was complete the ether layer was washed free of acid and then evaporated on a steam-bath until all the ether had been removed. A 98.7-g. portion of the siloxane so obtained was mixed with 98.7 g. of hexamethyldisiloxane and 4 ml. of concentrated sulfuric acid. This mixture was placed in a glass-stoppered bottle and shaken vigorously at room temperature for 24 hours. Then the oil was washed to free it of acid and distilled to remove the excess hexamethyldisiloxane (about 80 cc. recovered). This oil had a viscosity of 55.0 ctks. at 100°F. and 8.61 ctks. at 210°F.

Anal. Found: Cl, 16.9, 16.7, 16.9.

Equilibrated Methyl-*m*-chlorophenylsilicone Oil.—A sample (353.5 g.) of polymethyl-*m*-chlorophenylsiloxane was prepared by hydrolysis of methyl-*m*-chlorophenyldichlorosilane in an ice–water–ether system.

Anal. Calcd. for $[C_7H_7SiClO]_x$: Cl, 20.8. Found: Cl, 20.4.

An equilibrated oil was prepared by the reaction of 353 g. of polymethyl-*m*-chlorophenylsiloxane with 353 g. of hexamethyldisiloxane in the presence of 9 ml. of concentrated sulfuric acid. The method of carrying out the reaction and recovery of the desired oil is essentially the same as that described for methyl-*p*-chlorophenylsilicone oil. The viscosity of the final oil was 37.1 ctks. at 100°F. and 8.21 ctks. at 210°F.

Anal. Found: Cl, 18.1, 18.2.

1,3,5-Tris-*p*-chlorophenyl-1,3,5-trimethylcyclotrisiloxane.—In the preparation of polymethyl-*p*-chlorophenylsiloxane by the hydrolysis of methyl-*p*-chlorophenyldichlorosilane it was noted that a white crystalline solid was formed. This crystalline product was recrystallized from glacial acetic acid and shown to be 1,3,5-tris-*p*-chlorophenyl-1,3,5-trimethylcyclotrisiloxane, m.p. 125–126°.

Anal. Calcd. for $C_{21}H_{21}Si_3Cl_3O_3$: C, 49.3; H, 4.14; Cl, 20.8; mol. wt., 512. Found: C, 49.5; H, 5.0; Cl, 20.2; mol. wt., 512, 510.

Acknowledgment.—The author wishes to acknowledge the aid given by Mr. M. C. Agens for test data from the Shell Four Ball Wear Tester; Mr. L. B. Bronk, Mrs. M. Lennig and Mrs. D. G. Riekert for analytical data; and to Dr. J. R. Ladd for aid in the preparation of several of these compounds.

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[1] W. I. Patnode and D. F. Wilcock, THIS JOURNAL, **68**, 358 (1946).

[2] (a) F. S. Kipping and L. L. Lloyd, *J. Chem. Soc.*, **79**, 449 (1901); (b) J. F. Hyde and R. C. DeLong, THIS JOURNAL, **63**, 1194 (1941).

Preparation of Deuteroporphyrin IX Dimethyl Ester[1]

BY T. C. CHU AND EDITH JU-HWA CHU

RECEIVED JULY 31, 1952

As described in the literature, deuteroporphyrin IX dimethyl ester is generally prepared from hemin

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[1] This investigation was supported by a research grant from The National Institutes of Health, Public Health Service.