Spectral analysis of the diphenylvinylsilane cyclic dimer showed clearly the presence of 1,1,3,3-tetraphenyl-2-methyl-1,3-disilacyclopentane (IVc) to the exclusion of the other possible isomer (IIIc). The expected quartet and doublet from HC—CH$_3$ appeared at relatively low and high field, respectively, and bracketed neatly the single resonance peak from the two equivalent methylene groups.

The results from the related polymer were not so definite. However, the apparent absence of a doublet signal from CH$_3$—CH indicated that Vc is probably not present, thereby suggesting that the most likely structure is IIc.

The spectrum of the methylphenylvinylsilane cyclic dimer showed a split phenyl signal at low field, indicating the presence of both of the two possible structures. At high field were observed, successively, an incompletely resolved multiplet due to all the methylene groups present, a group of low peaks, probably from CH$_3$—CH, and another multiplet due to non-equivalent protons in the CH$_3$—Si groups. The multiple splittings were attributed to *cis* and *trans* isomers of both IIId and IVd. By comparing the relative areas of the two portions of the phenyl signal, it was established that this dimeric material is a 60:40 mixture of the two ring structures. However, the resonance peaks from CH$_2$ and CH$_3$—CH were not sufficiently well resolved to permit a conclusion as to which isomer constitutes the larger portion.

On the basis of the meager information available from the spectrum of the methylphenylvinylsilane polymer, structure IId is favored over the isomeric Vd, although the latter cannot be completely ruled out. Even in carbon tetrachloride solution the resonance peaks were viscosity broadened, and while the small quartet pattern from CH$_3$—CH did not appear to be present in high field, it might have been obscured by the other broad signals near this region.

In summary, the NMR evidence, while not always clear cut, did show that both five- and six-membered ring structures are represented among the various cyclic dimers, and in the main, appeared to reaffirm the earlier assigned[1] polysilethylene structure for the polymers.

EXPERIMENTAL[3,4]

Nuclear magnetic resonance spectra. The NMR spectra were determined using the Varian Associates High Resolution Spectrometer (V-4300-C), operated at 60 mc. and 14090 gauss. The spectra of all of the polymers and of diphenylvinylsilane cyclic dimer were run in carbon tetrachloride solution. The other cyclics (liquids) were run without solvent.

Physical properties. In Tables I and II are listed certain physical properties. The values shown have either not been reported previously or constitute revisions of those recorded earlier.[1]

TABLE I

Reaction product	n_D^{25}	d_4^{25}	R_D, Calcd.	R_D, Found
Dimethylvinylsilane:				
Polymer	1.4903	0.8827	0.3263	0.3277
Diethylvinylsilane:				
Polymer	1.4988	0.8970	0.3276	0.3272

TABLE II

Reaction Product	Mol. Wt., Calcd.	Mol. Wt., Found	Average Degree of Polymerization
Dimethylvinylsilane:			
Polymer	—	2340, 2190, 2110	25.6
Cyclic Dimer	172	178, 177	—
Diethylvinylsilane:			
Polymer	—	992, 980	8.6
Cyclic Dimer	228	239, 237	—
Diphenylvinylsilane:			
Polymer	—	647, 661	3.1
Methylphenylvinylsilane:			
Polymer	—	847, 864	5.8
Cyclic Dimer	297	283, 286	—

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[3] Calculated specific refractivities were computed from bond refractivity values listed in the following references: A. I. Vogel, W. T. Cresswell, G. H. Jeffery, and J. Leicester, *Chem. & Ind.* (*London*), 358 (1950), and A. I. Vogel, W. T. Cresswell, and J. Leicester, *J. Phys. Chem.*, **58**, 174 (1954).

[4] All molecular weight determinations were carried out cryoscopically in benzene.

An Evaluation of the Gilman-Haubein Determination of Alkyllithium

KENNETH C. EBERLY

Received August 18, 1960

The question arose concerning the application of the double titration of Gilman and Haubein[1] to assay of pure butyllithium under oxygen- and moisture-free conditions. It was felt that quantitative experiments were in order to confirm the method.

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[1] H. Gilman and A. H. Haubein, *J. Am. Chem. Soc.*, **66**, 1515–16 (1944).

EXPERIMENTAL

Butyllithium solution was prepared under conditions as dry and air-free as possible. In a 1-l. flask fitted with condenser, stirrer, graduated dropping funnel, batch thermometer, argon inlet, and water bath, 33.20 g. of Foote's 52.5% lithium dispersion (2.500 g.-atoms) was dispersed in 500 ml. of sulfuric acid-washed, sodium-dried heptane (Phillips' 99%) in a gentle current of argon. In the course of 55 min. 115.7 g. (1.250 moles) of 1-chlorobutane (n_D^{20} 1.4019) was added dropwise, the batch temperature varying between 35 and 43°. The slurry was stirred for another 30 min. at 35°, then quickly discharged into a baked, argon-filled, 28-oz. beverage bottle (capped under a slight positive pressure of argon). After the whole had settled for 100 hr. 512 ml. of colorless butyllithium solution was forced with argon pressure into a second baked, lamp nitrogen-filled, 28-oz. beverage bottle (capped under slight positive pressure of lamp nitrogen).[2]

One gallon of anhydrous ether (Baker and Adamson) was treated with 25 g. of sodium ribbon; then it was confined under argon for 50 days. Benzyl chloride (Baker and Adamson, reagent) was distilled in vacuum over phosphorus pentoxide, then stored over anhydrous calcium chloride under argon.

Exactly 1.00 ml. of clear butyllithium solution titrated 8.87 ml. of 0.19850*N* hydrochloric acid to the faintest Methyl Orange change.

Three 60-ml. bottles with serum caps were baked at 110°, then flushed with argon (using #19 and #20 hypodermic needles) until cool. Exactly 1.5 ml. of benzyl chloride and 10, 20, and 30 ml. of dry ether (from hypodermic syringes and needles baked at 110° and cooled over phosphorus pentoxide) were charged through the serum cap, respectively. After mixing, 1.00 ml. of colorless butyllithium solution was charged to each bottle through the serum cap. After reacting for 2 min., 5 ml. of water was added to each. Each was titrated with 0.19850*N* hydrochloric acid, first against phenolphthalein then Methyl Orange (faintest change). The titrations against Methyl Orange were 0.40, 0.43, and 0.46 ml., respectively.

The above experiment was repeated using lamp nitrogen instead of argon as the flushing agent. The titrations were 0.34, 0.37, and 0.40 ml., respectively.

Ten milliliters of sodium-dried ether contained enough oxygen, moisture, and ethanol to destroy butyllithium equivalent to 0.03 ml. of 0.19850*N* hydrochloric acid.

One milliliter of ball-milled lithium butoxide dispersion in dry heptane (titn., 4.07 ml. of 0.19850*N* hydrochloric acid) was treated with 1.8 ml. of dry benzyl chloride and 10 ml. of dry ether at 45–50° for 2 min. After dilution with water the titration remained unchanged.

CALCULATIONS AND CONCLUSIONS

Taking the best figure from a determination in lamp nitrogen, 8.87 ml. (total titn.) − 0.34 ml. (titn. after BzCl) + 0.03 ml. (ether corr.) × 100%/8.87 ml. (total titn.) or 96.5% of the base in the colorless butyllithium solution was destroyed by benzyl chloride. Since lithium butoxide is unaffected by benzyl chloride in ether in 2 min. at 45–50°, it is reasonable to believe that 96.5% of the total base in the clear butyllithium solution was carbon-bound lithium. One could assume that if butyllithium free from lithium butoxide and hydroxide could be prepared, benzyl chloride in absolutely dry and oxygen-free ether would destroy all of the alkalinity in it. The author feels that the method of Gilman and Haubein for assay of alkyllithium is most reliable.

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[2] Lamp nitrogen is almost completely dry and free from oxygen while commercial argon is not. However, lamp nitrogen reacts fairly rapidly with lithium dust at room conditions to yield lithium nitride, but it has no effect upon butyllithium over a period of 8 months.

A Study of Reaction Variables in Aromatic Chlorination by Antimony Pentachloride[1]

Peter Kovacic and Allen K. Sparks[2]

Received August 4, 1960

Our previous investigations[3] on aromatic chlorination by antimony pentachloride have been concerned primarily with the reaction mechanism. This report presents a study of reaction variables in the chlorination of aromatic compounds, particularly chlorobenzene, by antimony pentachloride. The aspects dealt with include solvent and catalytic effects, mode of addition, temperature, and time. In addition, the practicality of chlorination by this method was investigated.

The presence of nitrobenzene as a solvent in the chlorobenzene reaction, while ineffective in altering the isomer distribution significantly, necessitated the use of more drastic conditions to effect chlorination. Pyridine inhibited the reaction completely. These effects are attributed to the formation of addition compounds from antimony pentachloride and the solvents, resulting in deactivation of the metal halide. In fact, solid separated initially from solution in both cases, in accord with reports that antimony pentachloride forms complexes with pyridine[4] and nitrobenzene.[5] With titanium tetrachloride solvent, it is not known whether the increased temperature required for reaction is due to complexing or to a concentration influence.

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(1) Part IX of a series on "Reactions of Metal Halides with Organic Compounds"; from the Ph.D. thesis of A. K. Sparks, Case Institute of Technology, 1960.

(2) Allied Chemical Corporation Fellow, 1958–1960.

(3)(a) P. Kovacic and N. O. Brace, *J. Am. Chem. Soc.*, **76**, 5491 (1954); (b) P. Kovacic and A. K. Sparks, *J. Am. Chem. Soc.*, **82**, 5740 (1960).

(4) J. C. Hutton and H. W. Webb, *J. Chem. Soc.*, 1518 (1931).

(5) T. Maki and M. Yokote, *J. Soc. Chem. Ind., Japan*, **39** (suppl.), 442 (1936); *Chem. Abstr.*, **31**, 4499 (1937).