

**Acetates of Desylamine. Monoacetate.**—The monoacetate of desylamine<sup>12</sup> was prepared by the method used for the preparation of the monoacetate of 2,4,6-trimethyl-desylamine; m. p. 135–136°.

*Anal.* Calcd. for C<sub>18</sub>H<sub>19</sub>O<sub>2</sub>N: C, 75.87; H, 5.97; N, 5.53. Found: C, 76.12; H, 5.89; N, 5.51.

**Triacetate.**—Five grams of desylamine hydrochloride was heated on a steam-bath for eight hours with 50 cc. of acetic anhydride and 10 cc. of dry pyridine. At the end of this time 200 cc. of water was added and the mixture was stirred until the anhydride had decomposed. The aqueous portion was decanted and the gummy residue was washed with water. The gum was dissolved in 125 cc. of ligroin, and the solution was treated with Norit and filtered. After standing for twenty hours, the precipitate was collected on a filter and recrystallized from four volumes of methanol; m. p. 130–131°.

*Anal.* Calcd. for C<sub>20</sub>H<sub>19</sub>O<sub>4</sub>N: C, 71.20; H, 5.68; N, 4.15. Found: C, 71.20; H, 5.62; N, 4.05.

RESULTS OF THE "GRIGNARD MACHINE" ANALYSES<sup>7</sup>

Compound	Reaction time	Active hydrogen	Addition
2,4,6-Trimethyl-desylamine hydrochloride	10 min. <sup>a</sup>	3	0
2,4,6-Trimethyl-desylamine monoacetate	1 hr.	2	0
2,4,6-Trimethyl-desylamine triacetate <sup>b</sup>	1 hr.	0	4
$\beta$ -Isodurylaldehyde cyanohydrin	10 min.	1	1
Desylamine monoacetate	1 hr.	1	1

<sup>a</sup> Upon prolonged heating the value of the active hydrogen approached 4. <sup>b</sup> The reaction mixture yielded the monoacetate upon being worked up.

(12) Davidson, Weiss and Jelling. *J. Org. Chem.*, **2**, 319 (1937).

**Hydrolysis of 2,4,6-Trimethyl-desylamine and of Desylamine.**—(a) A mixture of 1 g. of the amine hydrochloride, 5 cc. of water, 5 cc. of concentrated hydrochloric acid, and 10 cc. of ethanol was heated at 95° in a sealed tube under nitrogen for twenty hours. Benzoin in a 40% yield separated and was collected on the filter. Under the same conditions 2,4,6-trimethyl-desylamine was unaffected.

(b) Same as (a) except heated at 130° for twenty-four hours. Desylamine gave a quantitative yield of benzoin. 2,4,6-Trimethyl-desylamine yielded 20% of a mixture of 2,4,6-trimethylbenzoin and 2,4,6-trimethylbenzil.

### Summary

1. 2,4,6-Trimethyl-desylamine has been prepared by the reaction of phenylmagnesium bromide with  $\beta$ -isodurylaldehyde cyanohydrin and also by the reduction of isonitroso-2,4,6-trimethyl-desoxybenzoin.

2. The reactions of 2,4,6-trimethyl-desylamine and desylamine with dilute hydrochloric acid were compared.

3. The autoxidation rate of 2,4,6-trimethyl-desylamine was compared with that of desylamine.

4. The mono- and triacetate of 2,4,6-trimethyl-desylamine were prepared and their reactions with dilute hydrochloric acid and with methylmagnesium iodide were studied.

5. The results obtained were ascribed to the propensity toward enolization shown by acetomesitylene derivatives.

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## Tri-*o*-tolyltin and the Instability of Organo-metallic Free Radicals

BY HUMBERT MORRIS, WARD BYERLY AND P. W. SELWOOD

Previous magnetic measurements on triphenylgermanium,<sup>1</sup> triphenyllead,<sup>2</sup> trimethyltin<sup>3</sup> and tricyclohexyllead<sup>3</sup> have shown that all these compounds exist in the diamagnetic or dimeric state. Molecular weight measurements by others have, on the contrary, consistently indicated partial or complete dissociation to the free radical. These results raise two questions: first, why do these compounds not exist as free radicals and, second, why do the magnetic measurements contradict the molecular weight measurements?

A possible answer to the first question is to be

(1) Selwood, *THIS JOURNAL*, **61**, 3168 (1939).

(2) Preckel and Selwood, *ibid.*, **62**, 2765 (1940).

(3) Morris and Selwood, *ibid.*, **63**, 2509 (1941).

found in the much larger radius of the metal atoms as compared with carbon, as in triphenylmethyl. It has been suggested<sup>3</sup> that the increased radius leads to a much greater number of effective collisions leading to formation of the dimer, and that a compound such as tri-*o*-tolyltin, in which steric effects are large, might exist as a free radical. This hypothesis is tested in the work reported here.

An effort to answer the second question by repeating ebulliometric measurements on trimethyltin and on triphenyllead is also reported.

### Experimental Part

**Magnetic Measurements.**—The magnetic susceptibilities were measured on the Gouy balance previously de-

scribed.<sup>4</sup> Measurements were made at 25 and 80°, benzene being used as the solvent. A field strength of about 13,100 oersteds was used throughout.

**Ebulliometric Measurements.**—These were made by means of a Swietoslawski differential ebulliometer.<sup>4</sup> The temperature differences were measured with an 8-junction thermocouple.

**Preparation of Tri-*o*-tolyltin.**—*o*-Bromotoluene was prepared from *o*-toluidine by diazotization and the Sandmeyer reaction.<sup>5</sup> Tetra-*o*-tolyltin was made by treating the Grignard reagent with stannic chloride. The Grignard reagent from 150 g. (0.88 mole) of *o*-bromotoluene and 21.5 g. of magnesium was refluxed with 33 g. (0.14 mole) of stannic chloride for twelve hours in ether. Water and dilute hydrochloric acid were added, and the ether evaporated off. The sludge was filtered dry and then refluxed in benzene to dissolve the tetra-*o*-tolyltin. The benzene solution was filtered and concentrated. White, powdery crystals were formed as the red-brown solution cooled. Two crops of crystals were obtained and recrystallized; yield, 15 g. ( $\frac{1}{30}$  mole); melting point 200–215°. According to Krause and von Grosse<sup>6</sup> the melting point of tetra-*o*-tolyltin is 214–215°.

Tri-*o*-tolyltin bromide was prepared according to the method of Chambers and Scherer.<sup>7</sup> The tetra-*o*-tolyltin was dissolved in chloroform and treated with 6.5 g. of iodine. It was then shaken with 30% sodium hydroxide to convert it to the hydroxide and to remove di-*o*-tolyltin oxide, which is water-soluble. The water layer was separated, and the bromide was formed by shaking with dilute hydrobromic acid. The (*o*-tolyl)<sub>3</sub>SnBr crystallizes with difficulty from chloroform, but it separates readily from petroleum ether; yield 1.5 g.; melting point 94–96°. The melting point is 97.5° according to Krause and von Grosse.<sup>6</sup>

The (*o*-tolyl)<sub>3</sub>SnBr does not react with molecular silver; 0.1 g. of the halide was shaken with 0.1 g. of molecular silver for two hours. It was filtered and recrystallized from petroleum ether. The melting point of the product was 89–93°.

The halide was reacted with sodium in absolute alcohol, according to the method of Krause and Becker.<sup>8</sup> The halide in 18 cc. benzene was treated with 18 cc. of alcohol and 2 g. of sodium. Then it was shaken with water. The benzene layer was separated, washed, dried, concentrated, and cooled in snow. A fine white powder was obtained which melted at 208–212°. After recrystallization from petroleum ether, the melting point was 208–210°; yield, 0.25 g. It was dried in vacuum at 50°.

A molecular weight determination in freezing benzene gave the following results

Molality (as R <sub>6</sub> Sn <sub>2</sub> )	0.0175	0.0278	
Apparent mol. wt.	664	825	±30

The molecular weight calculated for (*o*-tolyl)<sub>3</sub>Sn<sub>2</sub> is 784.

(4) Swietoslawski "Ebulliometry," Chemical Publishing Co. of New York, Inc., N. Y., 1937, p. 6.

(5) "Organic Syntheses," Collective Vol. 1, edited by Gilman, John Wiley and Sons, Inc., New York, N. Y., 1932, p. 130.

(6) Krause and von Grosse, "Die Chemie der Metall-organischer Verbindungen," Gebrüder Borntraeger, Berlin, 1937, p. 320.

(7) Chambers and Scherer, THIS JOURNAL, **48**, 1054 (1926).

(8) Krause and Becker, *Ber.*, **53B**, 188 (1920).

For reasons to be discussed below not much consideration should be given the molecular weight determination.

Analyses by T. S. Ma of the University of Chicago.

	Calculated for ( <i>o</i> -tolyl) <sub>3</sub> Sn <sub>2</sub> , %	Found, %	
Sn	30.4	29.73	29.95
H	5.4	5.19	5.20
C	64.4	63.27	63.16

This compound does not appear to have been previously reported.

## Results

In order to treat the data it is necessary to know the diamagnetic susceptibility of hexa-*o*-tolyliditin. The amount of this substance available was too small for direct measurement. The susceptibility was, therefore, calculated from Pascal's constants and the known susceptibility of hexamethylditin.<sup>3</sup> The susceptibility of this compound is  $-0.51 \times 10^{-6}$  and the molar diamagnetism is  $-167 \times 10^{-6}$ . The molar diamagnetism of quadricovalent tin is, therefore, nearer 39 than the usually accepted value of 30.<sup>9</sup>

For six phenylene groups plus six methyl groups the constants are  $(6 \times 49.3) + (6 \times 14.85) \times 10^{-6} = 384.9 \times 10^{-6}$ . Two quadricovalent tin atoms raise this to  $462.9 \times 10^{-6}$ . This number divided by the molecular weight gives  $-0.59 \times 10^{-6}$  as the susceptibility of hexa-*o*-tolyliditin per gram. Even if this value is as much as ten per cent in error it will not seriously affect the validity of the conclusions to be drawn from the work described here.

In the following table the susceptibilities of the solution are calculated for zero dissociation and for complete dissociation. These data are compared with the observed susceptibilities. Methods of calculation are given elsewhere.<sup>2</sup>

TABLE I  
SUSCEPTIBILITY OF A 0.25 M SOLUTION OF TRI-*o*-TOLYLITIN IN BENZENE

Temp., °C.	Calcd. for zero diss. $\times 10^6$	Calcd. for com- plete diss. $\times 10^6$	Observed $\times 10^6$
25	-0.700	-0.638	-0.7003
80	-0.701	-0.659	-0.705

It is clear from this table that the compound exists as hexa-*o*-tolyliditin. At 25° as little as 2% dissociation could have been detected.

This work constitutes proof that steric considerations are in themselves insufficient to produce dissociation, although they may greatly modify

(9) Stoner, "Magnetism and Matter," Methuen and Co. Ltd., London, 1934, p. 470.

the degree of dissociation, as has been shown for the hexaarylethanes.<sup>10,11</sup> The work also increases the probability previously suggested<sup>3</sup> that no stable organo-metallic free radical has yet been prepared. The metal ketyls are, of course, dissociated, but the dissociation does not involve a metal-metal bond.

The question as to why organo-metallic free radicals are of such low stability remains unanswered. It is not simply a matter of relative sizes of metal and carbon atoms. It is apparently not a matter of relative electronegativities because tetraarylhydrazines are known to dissociate.<sup>12</sup> Whatever the underlying cause may be, it evidently inhibits the resonance, or other phenomenon, which is a necessary adjunct to free radical formation. The recent observation of Bauer and Beach [THIS JOURNAL, **64**, 1142 (1942)] on the structure of hexamethylethane suggests a clue to the instability of organo-metallic free radicals. They report a probable stretching of the central C-C bond to  $1.58 \pm 0.03 \text{ \AA}$ . It is possible that in hexaarylethanes still more stretching occurs with consequent weakening of the ethane bond. But in the cases of the organometallic compounds such as hexaphenylditin, the tin atoms are so large that no stretching of the Sn-Sn bond is necessary. There is, therefore, no weakening of the bond and no tendency to form free radicals. The same interpretation may be applied to the corresponding compounds of silicon, germanium and lead.

It may be worth noting that the known free radical forming elements are limited to carbon, nitrogen, oxygen, possibly sulfur, and chlorine. Thus paramagnetic molecules are formed by these elements, but the diboranes,<sup>13</sup> hexaaryldisilanes<sup>14</sup> and tetraaryldiarsines (*e. g.*, phenyl cacodyl),<sup>15</sup> which might be expected to dissociate, do not. Schönberg and Rupp<sup>16</sup> suggest that diphenylene disulfide may dissociate, while nothing is known of the tetraaryldiphosphines.

The remaining question is: why do the magnetic measurements contradict the molecular weight determinations? In this connection it should be pointed out that the dielectric measurements of Lewis, Oesper and Smyth<sup>17</sup> on tri-

phenyllead exclude the remote possibility of an electrolytic type of dissociation.

Ebulliometric measurements were made on benzene solutions of trimethyltin and triphenyllead with the results given in Tables II and III.

TABLE II

BOILING POINT ELEVATION PRODUCED BY 0.9418 G. OF  $(\text{C}_6\text{H}_5)_3\text{Sn}$  DISSOLVED IN 104 CC. OF BENZENE

Time in minutes after addition of solute	Boiling point elevation, °C.
10	0.076
15	.045
20	.045
35	.049
125	.023
305	.026
Calcd. elevation for the dimer	.089

TABLE III

BOILING POINT ELEVATION PRODUCED BY 1.0355 G. OF  $(\text{C}_6\text{H}_5)_3\text{Pb}$  IN 104 CC. OF BENZENE

Time in minutes after addition of solute	Boiling point elevation, °C.
10	0.049
25	.027
55	.024
145	.008
Calcd. elevation for the dimer	.073

It is clear from these results that decomposition rapidly occurs, and that, even during the ten-minute interval necessary for the apparatus to come to equilibrium, considerable destruction of the compound must take place. In no case was the apparent molecular weight less than that of the dimer. During the test on triphenyllead a visible precipitate was formed during the first 30 minutes. It is, therefore, obvious that ebulliometric measurements are of as little value for the study of organo-metallic free radicals as they are for hexaarylethanes.<sup>18</sup> No attempt was made to determine the nature of the decomposition products from these compounds, but it is possible that they were similar to those reported by Calingaert, Soroos and Shapiro<sup>19</sup> as disproportionation products of  $\text{R}_6\text{Pb}_2$  compounds.

### Summary

Tri-*o*-tolyltin has been prepared and shown by magnetic measurements to be dimeric. Ebulliometric measurements on solutions of trimethyltin and of triphenyllead emphasize the unreliability of such methods for the study of free radicals.

EVANSTON, ILLINOIS

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(10) Roy and Marvel, THIS JOURNAL, **59**, 2622 (1937), *et seq.*

(11) Preckel and Selwood, *ibid.*, **63**, 3397 (1941).

(12) Weitz and Müller, *Ber.*, **68B**, 2306 (1935).

(13) Farkas and Sachsse, *Trans. Faraday Soc.*, **30**, 331 (1934).

(14) Schlenk, Renning and Racky, *Ber.*, **44**, 1178 (1911).

(15) Schlenk, *Ann.*, **394**, 216 (1912).

(16) Schönberg and Rupp, *Naturwiss.*, **21**, 561 (1933).

(17) Lewis, Oesper and Smyth, THIS JOURNAL, **62**, 3243 (1940).

(18) Preckel and Selwood, forthcoming publication.

(19) Calingaert, Soroos and Shapiro, THIS JOURNAL, **64**, 462 (1942).