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The Infrared Spectra of Alkylithium Compounds

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The infrared spectra of methylithium, ethyllithium and phenyllithium have been investigated in the region 300–4000 cm^{-1} . Results upon substitution of lithium-6 for lithium-7 and of deuterium for hydrogen in methylithium show that previous assignments of bands in the 800–1000 cm^{-1} region to carbon–lithium fundamental stretching modes are in error. The only bands found which involve the motion of lithium atoms occur between 350 and 570 cm^{-1} ; these appear to represent complex modes of vibration in polymeric species. The bonding in organolithium compounds is discussed in the light of the spectral evidence.

Recently two groups of workers have investigated the infrared spectra of organolithium compounds in the 700–4000 cm^{-1} region and have drawn conclusions about the structure and association of these compounds based on their interpretation of these spectra. The first investigation was that of Brown and Rogers, who studied spectra of methylithium and ethyllithium as Nujol mulls, and of ethyllithium in benzene solution.¹ They assigned bands at 880 cm^{-1} to carbon–lithium fundamental stretching vibrations in monomeric species and bands at 925 cm^{-1} to similar vibrations in polymers.

More recently Rodionov, Shigorin and their co-workers have investigated the infrared spectra of methylithium and ethyllithium in the vapor phase² and of a great variety of organolithium compounds as solids and in solution.³ Their assignments all depend on the complete vibrational assignment proposed for CH_3Li , assumed to be monomeric in the vapor and to have C_{3v} symmetry.² A band at 1052 cm^{-1} was attributed to the C–Li fundamental stretching mode. Accordingly, a recurring band near 1050 cm^{-1} (not assigned by Brown and Rogers) was attributed to the C–Li fundamental in all organolithium compounds, and bands in the 850–930 cm^{-1} region were attributed to C–Li modes in various polymers.

The total lack of agreement between the two previous groups of workers suggested our reinvestigation of the infrared spectra of organolithium compounds. In this work the region studied has been extended to 300 cm^{-1} , and lithium and hydrogen isotopes have been substituted as an aid in making assignments. None of the bands above 600 cm^{-1} in any of the three compounds studied shift detectably upon substitution of Li^6 for Li^7 . A calculation based on the simple harmonic oscillator approximation predicts a shift of about 50 cm^{-1} for this isotopic substitution in a C–Li fundamental stretching band with a frequency of about 1000 cm^{-1} .⁴ Since a shift as small as 2 cm^{-1} would

have been detected, it is apparent that none of the absorption bands in the sodium chloride region can represent C–Li modes and that therefore both of the previous (conflicting) assignments of C–Li bands in this region are in error.^{1–3}

In the region below 600 cm^{-1} which was not studied by previous workers, bands are found which do shift upon substitution of Li^6 for Li^7 and hence must represent modes of vibration involving lithium. However, for reasons explained below, we believe that these bands represent complex modes of vibration in associated species rather than simple monomeric C–Li stretching bands.

Experimental

Infrared Spectra.—Most of the spectra were obtained with a Perkin-Elmer 112 single-beam spectrometer with sodium chloride or cesium bromide prism calibrated with water, ammonia, polystyrene and carbon dioxide. Reproducibility of band positions was ± 1 cm^{-1} in the region 300–2000 and ± 2 cm^{-1} from 2000 to 4000 cm^{-1} . Some spectra were also determined using a Baird spectrometer with sodium chloride prism, calibrated with polystyrene.

All of the compounds were studied as mulls in dry white petroleum oil (Stanolind) over the entire region from 300 to 4000 cm^{-1} . In addition, the methylithium and phenyllithium samples were studied as mulls in perfluoro-kerosene in the region 1300–4000 cm^{-1} , to eliminate complications from C–H bands in the mulling agent. Ethyllithium was also studied at various concentrations in benzene solution in cells at 0.1 mm. path length and as a vapor. The vapor spectra were determined in cells with 12 cm. path length with NaCl or CsI windows, which had been baked out at 120° for 24 hr. The cells were filled with argon before loading and then evacuated to about 1 mm. of argon pressure. For determination of the vapor spectra the cells were heated to about 80° in an aluminum block thermostat.

When the single-beam instrument was used, the spectrum of the solvent or mulling agent was obtained with identical instrument settings soon before or after the organolithium compound was studied. Values of I/I_0 were calculated for each organolithium spectrum by dividing the sample spectrum by that of the solvent or mulling agent point for point. Some of the results are shown in Fig. 1.

The samples were prepared and loaded into cells in a dry-box under an atmosphere of dry nitrogen or argon, immediately before determining the spectra. Nevertheless, some bands observed in mull spectra around 900 cm^{-1} varied in relative intensity in successive runs, probably from hydrolysis or oxidation occurring during sample preparation or spectral determination. Mull spectra were run several times on several preparations of each compound in order to minimize this difficulty.

Preparation of Organolithium Compounds.—Lithium-6 metal (99.3% isotopically pure) was purchased from Union Carbide Nuclear Corporation. Lithium ribbon (97.3% Li^7) from the Lithium Corporation of America was used to prepare lithium-7 compounds.

Ethyllithium-6 and -7 were prepared from lithium sand

(1) T. L. Brown and M. T. Rogers, *J. Am. Chem. Soc.*, **79**, 1859 (1957).

(2) A. N. Rodionov, D. Shigorin, T. Talalaeva and K. Kocheshkov, *Izvest. Akad. Nauk. S.S.S.R., Otdel. Khim. Nauk*, **120** (1958); D. N. Shigorin, T. V. Talalaeva, K. A. Kocheshkov and A. N. Rodionov, *Izvest. Akad. Nauk. S.S.S.R., Ser. Fiz.*, **22**, 1110 (1958); D. N. Shigorin, *Spectrochim. Acta*, **14**, 198 (1959).

(3) A. N. Rodionov, D. N. Shigorin, T. V. Talalaeva and K. A. Kocheshkov, *Doklady Akad. Nauk. S.S.S.R.*, **123**, 113 (1958); A. N. Rodionov, V. N. Vasileva, T. V. Talalaeva, D. N. Shigorin, E. N. Gur'yanova and K. A. Kocheshkov, *ibid.*, **125**, 562 (1959); A. N. Rodionov, T. V. Talalaeva, D. N. Shigorin and K. A. Kocheshkov, *ibid.*, **128**, 819 (1959); A. N. Rodionov, G. V. Kazennikova, T. V. Talalaeva, D. N. Shigorin and K. A. Kocheshkov, *ibid.*, **129**, 951 (1959).

(4) The ratio of the frequencies should be proportional to the square roots of the reduced masses for C– Li^6 and C– Li^7 , or 1.052. See G. Herzberg, "Infrared Spectra of Diatomic Molecules," 2nd Ed., D. Van Nostrand Co., Princeton, New Jersey, 1950, p. 75.

and ethyl bromide in pentane,⁵ and the reaction mixture was transferred to the dry box. The pentane was removed by distillation under vacuum and hot benzene was added immediately. The mixture was filtered quickly through a sintered-glass disc. When the clear, very pale yellow filtrate was cooled, needles of ethyllithium crystallized. The crystals were filtered on a sintered-glass disc, washed with pentane and dried under vacuum.

Methylithium-6 and -7 were prepared by the metal-halogen exchange reaction between ethyllithium and iodomethane¹ in hexane solution. The methylithium precipitate was washed with pentane on a sintered-glass filter and dried under vacuum. Iodomethane-*d*₃ was obtained from the Volk Chemical Company and used similarly to prepare methylithium-*d*₃. Phenyllithium-6 and -7 were prepared by a similar metal-halogen exchange reaction from ethyllithium and bromobenzene in benzene.

Results

Methylithium.—In mulls of methylithium, two bands were observed in the C-H stretching region at the unusually low frequencies of 2840 and 2780 cm^{-1} , shifted to 2150 and 2027 cm^{-1} in CD_3Li (Table I). Bands above 2900 cm^{-1} , reported by earlier investigators,^{1,3} were not observed. The 2840 and 2780 cm^{-1} bands can be assigned to the asymmetric and symmetric C-H stretching modes, lowered by electron deficient Li-C-Li bonding. Brown and Rogers previously have pointed out that low frequency C-H stretching bands are characteristic of methyl groups involved in electron deficient bonding,¹ as in compounds like $[\text{Be}(\text{CH}_3)_2]_z$ and $\text{Al}_2(\text{CH}_3)_6$. The absence of bands in the usual C-H stretching position near 3000 cm^{-1} indicates that free methyl groups are not present in methylithium.

Absorption bands at 1480 and 1427 cm^{-1} occur in the protium compounds, shifted to 1100 and 1043 cm^{-1} in the deuterium compounds. The frequencies of those bands are in the right range for C-H bending vibrations⁶ and the shifts on deuterium substitution are consistent with this assignment. Bands are found at 1061 and 1096, which the Russian workers assigned to the symmetrical and unsymmetrical C-Li stretching modes.^{2,3} These bands do not shift on Li⁶ substitution and so cannot represent modes of vibration involving carbon and lithium to any significant extent. It is likely that these bands are also due to C-H rocking or deformation vibrations.

All of the six bands discussed so far are shifted upon deuterium substitution by an amount ($\nu_{\text{H}}/\nu_{\text{D}} = 1.30$ to 1.36) which indicates that they involve principally the motions of hydrogen atoms. These isotopic frequency ratios are comparable to those for the hydrogenic stretching and deformation vibrations in methyl chloride, which have $\nu_{\text{H}}/\nu_{\text{D}} = 1.31$ to 1.37.⁷

The bands between 870 and 930 cm^{-1} have been assigned by both earlier groups of investigators to C-Li stretching bands in polymeric species. We find that all of these bands vary widely in intensity in different preparations of methylithium. In a few samples they were absent entirely. They must therefore represent vibrations due to some impurity present in variable amounts in most

(5) K. Ziegler and H. Colonius, *Ann.*, **479**, 135 (1930).

(6) L. J. Bellamy, "The Infra-Red Spectra of Complex Molecules," 2nd Ed., Methuen and Company, London, 1958, Chapt. 2.

(7) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., New York, N. Y., 1945, p. 315.

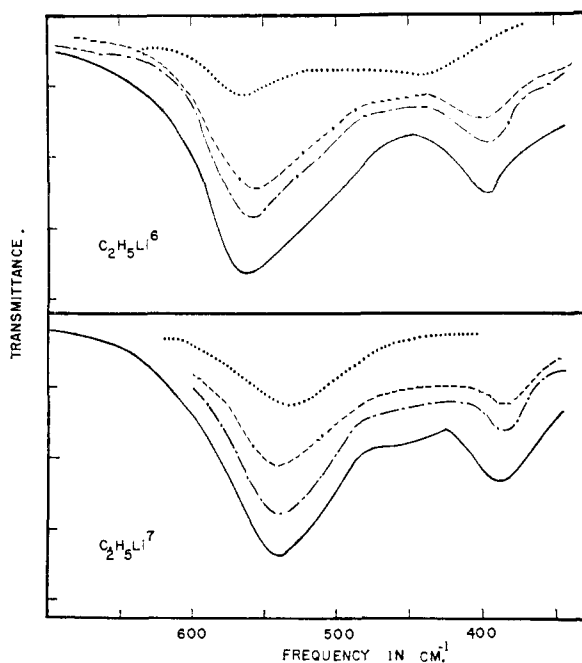


Fig. 1.—Spectra of ethyllithium determined with Perkin-Elmer Model 112 spectrometer with cesium bromide prism at 25°: vapor, 10 cm. path length, 80°; -----, 0.37 *M*; - · - · - ·, 0.53 *M*; ———, 0.75 *M* in benzene, 0.1 mm. path length.

methylithium preparations. From their position it seems possible that C-O vibrations in oxidation products are responsible for these absorption bands. The fact that these bands are not shifted upon substitution either of deuterium or lithium-6 is a further indication that they are not methylithium bands. The band at 1210 cm^{-1} also shows variable intensity and no isotopic shifts and so is probably also an impurity band.

Finally, two bands were discovered near 500 cm^{-1} which were not found by the previous investigators. These bands are significantly shifted to higher frequency upon lithium-6 substitution and so represent modes of vibration involving lithium. (The very low frequencies suggest that these bands are not due to simple C-Li stretching modes but rather to more complicated C-Li modes of polymeric methylithium species.) The frequency shifts upon lithium-6 substitution can be compared with the expected shift for harmonic C-Li bonds, which is about 26 cm^{-1} for bands with a frequency near 500 cm^{-1} .⁴ Although some of the bands appear to shift by approximately this amount, most show rather smaller shifts, as expected if they represent complex vibrational modes. Furthermore, these low-frequency bands shift substantially upon deuterium substitution ($\nu_{\text{H}}/\nu_{\text{D}} = 1.16$ and 1.26), indicating that they involve the motion of hydrogen as well as lithium.

Ethyllithium.—In the C-H stretching region, this substance has a pair of low frequency bands at 2760 and 2840 cm^{-1} , as does methylithium. In addition a band at 2940 cm^{-1} is found, in the proper region for a C-H asymmetric stretching vibration in the terminal methyl group, not influenced by electron-deficient bonding. The symmetric stretch-

ing band for the CH_3 group should occur near 2870 cm.^{-1} ⁶ and so probably overlaps with and contributes to the 2840 cm.^{-1} CH_2 stretching band, whose frequency is lowered by electron-deficient bonding.

In the C-H deformation region a weak band occurs at 1450 cm.^{-1} . A sharp peak is found at 1385 cm.^{-1} , which does not appear in methyl-lithium. This band is at just the right frequency for the C-H symmetrical bending mode in methyl groups.⁶ The occurrence of this diagnostic band in ethyllithium, and its absence in methyllithium is a further indication that free methyl groups exist in the former compound but not in the latter. A pair of bands is found at 1050 and 1098 cm.^{-1} corresponding to similar bands in methyllithium assigned to C-H deformations (*vide supra*).

Bands were observed in the 870 – 950 cm.^{-1} region in mulls of ethyllithium, just as for methyllithium. These bands also appeared in our vapor spectra, although the Russian workers do not report bands in this region in ethyllithium vapor. It seems probable that absorption in this region is due to impurities in ethyllithium as in methyllithium. If so, the vapor spectra indicate that one of these impurities is quite volatile. It is also possible, however, that these bands represent, in part, skeletal deformations in the C_2H_5 groups.⁶

None of the bands described above shifts upon substitution of Li^6 for Li^7 . Bands which do shift upon lithium isotope substitution occur in the region from 340 to 570 cm.^{-1} , their position depending somewhat on the physical state of the compound. In benzene solution the bands were found at 560 and 398 cm.^{-1} for $\text{C}_2\text{H}_5\text{Li}^6$ and at 538 and 382 cm.^{-1} for $\text{C}_2\text{H}_5\text{Li}^7$. The relative intensities of the C-Li bands are not strongly concentration-dependent (Fig. 1). The position of these bands appears rather similar in the vapor spectra. Band positions and intensities are shifted somewhat in the mulls of solid ethyllithium, however. It is possible that the type of polymerization of the ethyllithium may be different in the solid than in the vapor and in solution.

Phenyllithium.—The spectra of solid phenyllithium samples show a C-H stretching band in the normal position for an aromatic ring and also a low frequency band at 2750 cm.^{-1} . The bands between 1300 to 2000 cm.^{-1} probably represent C-H and skeletal modes of the type usually found for aromatic compounds.⁸ Phenyllithium shows two bands at 1110 and 1050 cm.^{-1} , very close to the similar pairs observed for methyllithium and ethyllithium and attributed to C-H deformations.

A series of bands appear at 615 – 762 cm.^{-1} which probably represent C-H out-of-plane deformations. These bands can be distinguished from C-Li absorption bands because, like all of the higher frequency bands, they are not shifted upon Li^6 substitution. Bands which do involve the motion of lithium atoms are found at 421 and 378 cm.^{-1} in phenyllithium-7 and at slightly higher frequencies in phenyllithium-6.

(8) L. J. Bellamy, ref. 6, Chapt. 5.

Discussion

The spectral results for isotopically-substituted molecules (Table I) establish that the previous assignments of bands in the 800 – 1100 cm.^{-1} region as C-Li stretching modes¹⁻³ are in error. Infrared absorption in this region, and in fact all absorption in the sodium chloride region, appears to be due either to modes of vibration which do not involve lithium or to impurities. Extensive studies of spectra of higher organolithium compounds have been carried out by Rodionov, Shigorin, *et al.*, and published in a series of seven papers.^{2,3} Spectral interpretations in those papers all depend on the assignment of the 1052 cm.^{-1} band in methyllithium to the C-Li fundamental stretching mode. It is evident that this entire body of work will now have to be reinterpreted.

The unexpectedly low frequencies of the C-Li bands and their behavior on isotopic substitution strongly suggest that they represent complex modes of vibration in polymeric molecules rather than simple C-Li stretching vibrations. Organolithium compounds are known to be strongly associated in solution,^{1,9} and recently it has been shown that ethyllithium is polymeric even in the vapor phase.¹⁰ This finding is substantiated by the vapor spectrum of ethyllithium which is markedly similar to the mull and solution spectrum even in the C-Li region.

TABLE I
FREQUENCY MAXIMA FOR ORGANOLITHIUM
COMPOUNDS, CM.^{-1}

Methyllithium ^a				Ethyllithium ^a		Phenyl-lithium ^a	
CH_3Li^6	CH_3Li^7	CD_3Li^6	CD_3Li^7	$\text{C}_2\text{H}_5\text{Li}^6$	$\text{C}_2\text{H}_5\text{Li}^7$	$\text{C}_6\text{H}_5\text{Li}^6$	$\text{C}_6\text{H}_5\text{Li}^7$
				2940 ^{a,b}	2940 ^{a,b}	3000	3000
2840	2840	2150	2150	2840 ^{a,b}	2840 ^{a,b}	2750	2750
2780	2780	2027	2027	2760 ^{a,b}	2760 ^{a,b}	1960	1960
						1810	1810
						1600	1600
1480	1480	1100	1100	1450 ^a	1450 ^a	1460	1460
1427	1427	1043	1043				
				1383 ^{a,b}	1383 ^{a,b}		
						1280	1280
(1210)	(1210)	(1210)	(1210)				
1096	1096	827	827	1098 ^{a,b}	1098 ^{a,b}	1100	1100
1061	1061	815	815	1050 ^{a,b}	1050 ^{a,b}	1050	1050
(1025)	(1025)						
(923)	(923)	(923)	(923)	945 ^{a,b}	945 ^{a,b}		
(900)	(900)	(900)	(900)	920 ^b	920 ^b		
(867)	(867)			877 ^{a,b}	877 ^{a,b}	(880)	(880)
						762	762
						704	704
						670	670
						615	615
517	514	455	436	570 ^b	566 ^b		
				565 ^a	535 ^a		
446	417	348	336	496 ^a	465 ^a	429	421
				362 ^a	340 ^a	390	378

^a Bands observed in mulls. ^b Bands observed in vapor.

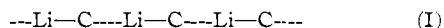
The previous vibrational analysis of methyllithium was based on the assumption that the vapor of this substance consisted of monomeric molecules with C_{3v} symmetry. However, it is unlikely that methyllithium vapor is monomeric. The C-Li infrared absorption in methyllithium vapor must

(9) G. Wittig, F. J. Meyer and G. Lange, *Ann.*, **571**, 167 (1951); F. Hein and H. Schramm, *Z. physik. Chem.*, **151**, 234 (1930).

(10) J. L. Berkowitz and T. L. Brown, private communication by T. L. Brown.

lie at frequencies outside the sodium chloride region, since all of the bands reported by Shigorin² have been shown not to be C-Li bands. Moreover, Shigorin's spectra of methyl lithium vapor show no sign of the rotational fine structure² which would be expected for molecules as simple as CH₃Li.

In their papers Rodionov and Shigorin describe the polymerization of organolithium compounds in terms of the formation of "lithium bonds" (I), analogous to hydrogen bonds, which bring about



cyclic or linear association of these compounds in solution.^{2,3} However, the strong association of alkyllithium compounds, persisting even in the

vapor phase, suggests (as Brown and Rogers earlier proposed¹) that association of organolithium compounds takes place through the formation of multi-center electron-deficient bonds of the same type which occur in Al₂(CH₃)₆ and Be(CH₃)_{2z}. In the light of the evidence now available, we see no reason for regarding the bonds in alkyllithium polymers as essentially different from other electron-deficient bonds or in designating them by a special name.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE 39, MASS.]

The Preparation of Organolithium Compounds by the Transmetalation Reaction. I. Vinyllithium^{1,2}

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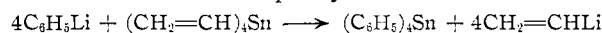
The transmetalation reaction occurring between phenyllithium and tetravinyltin (4:1 molar ratio) in ether produces vinyllithium in good yield. A similar reaction occurs between *n*-butyllithium and tetravinyltin in pentane; in this case solid vinyllithium precipitates. Vinyllithium is more stable in ether and tetrahydrofuran solution than are *n*-butyllithium or phenyllithium. The use of vinyllithium in the preparation of a number of previously known vinyl compounds, as well as of the new [B(CH=CH₂)₄]⁻ and [B(CH=CH₂)(C₆H₅)₂]⁻ ions, is described.

The exchange of organic groups between an organolithium compound and an organic derivative of a heavy metal (R₂Hg, R₃Tl, R₄Sn, R₄Pb, R₃Sb, R₃Bi) represents a route to organolithium reagents which up to the present time has had only very little synthetic application. Many examples of this reaction, which was reported first by Schlenk and Holtz,³ have been given. In nearly all examples cited, the lithium reagent produced in this exchange reaction was more conveniently prepared by the more common methods used in the synthesis of organolithium compounds.

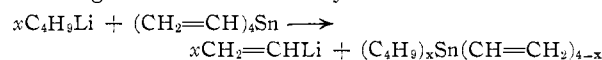
We have used the transmetalation reaction to prepare a number of novel organolithium reagents which are either difficult or impossible to prepare by other methods: vinyllithium,¹ allyllithium,⁴ perfluorovinyllithium⁵ and others. The present report is concerned with the preparation and some reactions of vinyllithium.⁶

We have found that the transmetalation reaction between a vinyltin compound and an alkyl- or aryllithium compound represents a very versatile procedure for preparing vinyllithium either in solution or in solid form. Most convenient for

most synthetic purposes is the preparation of vinyllithium in diethyl ether solution. The most practical starting material is tetravinyltin, which became available in developmental quantities⁷ during the late stages of this research. The reaction between phenyllithium and tetravinyltin (4:1 molar ratio) in ether solution proceeded essentially to completion within 30 minutes; tetraphenyltin precipitated in *ca.* 95% yield, and a solution of vinyllithium containing also lithium bromide (from the phenyllithium preparation) and minor amounts of tetraphenyltin⁸ remained



In some cases vinyllithium solutions free of these impurities were needed. This requirement was met when vinyllithium was prepared in pentane using *n*-butyllithium. Treatment of tetravinyltin with *n*-butyllithium in pentane also resulted in an exchange reaction. In the system



the organotin compounds and *n*-butyllithium are liquids soluble in pentane, while vinyllithium, a solid, is not very soluble in pentane and precipitates from solution. The solid vinyllithium can be filtered (under nitrogen: it is pyrophoric in air), washed free of soluble contaminants and dissolved in the desired solvent. This exchange reaction does not go to completion, and a butyllithium/

(1) Preliminary communication: D. Seyferth and M. A. Weiner, *Chemistry and Industry (London)*, 402 (1959).

(2) Also Part X of the series, "Vinyl Derivatives of Metals"; Part IX, D. Seyferth, G. Raab and K. A. Brändle, *J. Org. Chem.*, **26**, in press (1961).

(3) W. Schlenk and J. Holtz, *Ber.*, **50**, 262 (1917).

(4) D. Seyferth and M. A. Weiner, *J. Org. Chem.*, **24**, 1395 (1959).

(5) D. Seyferth, T. Wada and G. Raab, *Tetrahedron Letters*, No. 22, 20 (1960).

(6) A review of previous attempts to prepare vinyllithium is given by D. Seyferth in "Vinyl Compounds of Metals," in "Progress in Inorganic Chemistry," Vol. III, F. A. Cotton, editor, Interscience Publishers, Inc., New York, N. Y., 1961.

(7) The current suppliers are Metal and Thermit Corporation and Peninsular ChemResearch, Inc.

(8) Tetraphenyltin is soluble to the extent of 0.102 g. per 100 ml. of diethyl ether at 20°: W. Strohmeier and K. Miltenberger, *Chem. Ber.*, **91**, 1357 (1958).