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SYNTHESIS OF LITHIOMETHANES ($CH_{4-n}Li_n$) AND CHARACTERIZATION OF THE VAPOR SPECIES OF LITHIOMETHANES BY FLASH VAPORIZATION MASS SPECTROSCOPY *

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Summary

An extensive study of the reaction chemistry of halocarbons with high temperature lithium vapor is reported. New syntheses are reported for dilithiomethane and methyllithium, and an improved synthesis for tetralithiomethane has been developed. The new compound trilithiomethane has also been prepared.

Introduction

Since our report in 1972 [1] of the synthesis of tetralithiomethane, interest in the polylithiated methanes, $CH_{4-n}Li_n$, has steadily increased from both experimental and theoretical viewpoints.

Theoretical interest centers on elucidating the unusual structural geometries and bonding properties present in vapor phase species generated from such polylithium organic compounds. Spectroscopic studies of such species isolated in inert matrices are now underway [2].

Hoffmann has recently discussed the requirements for stabilizing planar carbon species [3]. Schleyer and Pople [4] have discussed and predicted the low lying energy state of *cis*-dilithiomethane and indicated that this species along with trilithiomethane and tetralithiomethane are excellent candidates for observation of the long sought anti-Le Bel and Van't Hoff simple planar carbon species. More extensive calculations carried out on dilithiomethane have shown dimeric [5] and trimeric [6] cluster species to be stable and a trimer species of D_{3h} symmetry is

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* Dedicated to Professor H.J. Emeléus on the occasion of his 80th birthday on 22nd June, 1983. R.J.L. has been a friend and admirer of Professor Emeléus and his work since their first meeting in the early stage of the Lagow laboratory. It has been our privilege to further develop some of the trifluoromethyl organometallic chemistry pioneered by Professor Emeléus and his students. We have selected this basic manuscript on multiple lithium substituted methanes to dedicate to Professor Emeléus. This field is in its early stages of development as was much of the best work from the Emeleùs laboratory.

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exceedingly stabilized by bridging lithium atoms [6]. More recently the gas phase structure of cations such as $CH_{5-n}Li_n^+$ and their likely high temperature decomposition modes have been examined [7,8].

Verification of these predictions has been hampered by the problems inherent in handling such lithiocarbon materials. These difficulties included extreme air and moisture sensitivity, lack of an observable vapor pressure below 650°C, thermal instability above 225°C, insolubility in inert polar organic solvents and purification problems.

Experimentally, a method for synthesizing extremely pure dilithiomethane suitable for characterization was reported [9]. Subsequent characterization of dilithiomethane by flash vaporization mass spectrometry [9] yielded in addition to monomers, small polymeric clusters ranging in size from dimers to tetramers. The finding of such ions indicates that calculations must begin to be made on polymeric species to accurately model their electronic states.

Solid phase NMR [10], ESCA [11], X-ray and neutron diffraction studies [12] were undertaken on $(CH_2Li_2)_n$ and $(CD_2Li_2)_n$ and preliminary results indicate that $(CH_2Li_2)_n$ may be trimeric in the solid state. In addition the CLi_5^+ cation was observed for the first time in the flash vaporization mass spectrum of CLi_4 [7].

Earlier we reported the first synthesis of tetralithiomethane from the reaction of carbon tetrachloride and lithium vapor in only 16% yield [1], with a number of by-products. Further experimentation has led to a more controlled synthesis of higher selectivity. In this manuscript, we present details for the synthesis of the entire series of lithiated methanes by lithium vapor techniques and flash vaporization mass spectral results of the composition of the vapor phase species.

A preliminary report describing the synthesis of trilithiomethane has appeared elsewhere [13]. Several trends (i.e., the number of lithium substituents, the selective activation of the C–H bond and the number of C_2 lithiated species observed among the chloromethane reaction products) are examined.

Experimental

CH_3Cl-lithium vapor reaction

All reactions were carried out in the stainless steel reactor illustrated in Fig. 1. In a 60-min reaction ca. 10 g of lithium metal (1.43 mol) vaporized at 750°C was cocondensed with CH_3Cl (43.3 mmol) on a liquid nitrogen cold finger. The cold finger was warmed to room temperature and the reactor opened under an argon atmosphere. The lithium product was removed from the cold finger, ground and sieved to produce a fine lithium free gray pyrophoric powder.

The reactive solid was slowly hydrolyzed with D_2O vapor over a two day period on a vacuum line. The hydrolysis gases were separated by GC (Bendix 2300 gas chromatograph) employing a phenyl isocynate/porasil C column and utilizing a temperature programmed gas chromatographic procedure. The individual compounds were identified and quantitated by comparison of their retention times and peak areas with authentic samples. The degree of deuteration (which corresponds to lithium substitution) and the identity of each species were determined by high resolution mass spectrometry (DuPont 21-110C). Mass spectral intensities were used to determine the percentages of each methane species. The results are listed in Table 1.

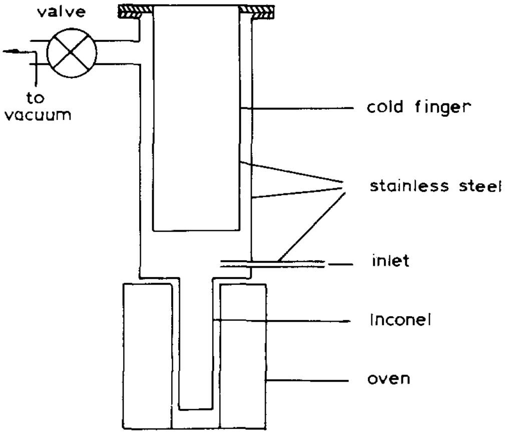

Fig. 1. Basic reactor.

CH_2Cl_2-lithium vapor reaction

Cocondensation of lithium vapor (1.43 mol) at 750 and at 850°C with CH_2Cl_2 (43.3 mmol) resulted in the isolation of a dark gray pyrophoric powder. Characterization was carried out in the manner previously described for the CH_3Cl-lithium vapor reaction. The results are listed in Tables 1 and 2.

$CHCl_3$-lithium vapor reaction

31.1 mmol of $CHCl_3$ was utilized in this reaction. Characterization of the black pyrophoric powder was carried out in the manner previously described for the monochloromethane reaction. The results are shown in Table 1.

TABLE 1

YIELDS OF PRODUCTS FROM THE VARIOUSLY CHLORINATED METHANE REACTIONS

Products	Substrate (%(mmol))			
	CH_3Cl	CH_2Cl_2	$CHCl_3$	CCl_4
CH_4	2.3 (0.6)	0.9 (0.2)	2.1 (0.4)	–
CH_3D	97.4 (26.1)	3.7 (0.9)	3.5 (0.6)	–
CH_2D_2	–	65.7 (16.8)	19.1 (3.9)	–
CHD_3	–	–	15.5 (3.1)	–
CD_4	–	–	20.1 (4.0)	40.5 (7.6)
C_2D_2	trace	29.7 (7.6)	39.7 (7.9)	58.5 (10.9)
C_2D_4	–	–	trace	trace
C_2D_6	–	–	–	trace

TABLE 2

YIELDS OF DEUTERATED PRODUCTS FROM THE REACTIONS OF CH_2Cl_2 WITH LITHIUM VAPOR (%)

Products	At 750°C	At 850°C
CH_4	0.9	–
CH_3D	3.7	11.8
CH_2D_2	65.7	44.5
CHD_3	–	0.6
CD_4	–	1.6
C_2D_2	29.7	40.4
C_2D_4	–	1.1
C_2D_6	–	–

The reactive solid was also derivatized by adding chlorotrimethylsilane to a −78°C THF solution of the reaction product and was warmed to room temperature then stirred over a 24-h period. Removal of the solvent by distillation yielded an oily residue, which was characterized using a temperature program gas chromatograph incorporating a 10% SE 30/chromosorb P column and low resolution mass spectrometry. Reference samples of bis-, tris-, and tetrakis(trimethylsilyl)methanes were prepared according to methods reported by Merker and Scott [14]. Mass spectral fragmentation patterns for the monosilyl, disilyl, trisilyl and tetrasilyl methanes have been reported by Dimmel [15]. The ^1H NMR spectra of the individual chromatographed fractions were identical to those obtained by Merker and Scott [14] for bis-, tris-, and tetrakis(trimethylsilyl)methanes.

CCl_4-lithium vapor reaction

Cocondensation of lithium vapor (1.43 mol) at 750 and at 800°C with CCl_4 (20.8 mmol) resulted in the isolation of a black pyrophoric powder. Characterization was carried out in the manner previously described for the CH_3Cl-lithium vapor reaction. The results are listed in Tables 1 and 3.

Hydrolysis of the lithiocarbon precursor with D_2O was used as the principal

TABLE 3

YIELDS OF DEUTERATED PRODUCTS FROM THE REACTIONS OF CCl_4 WITH LITHIUM VAPOR (%)

Products	At 750°C	At 800°C
CH_4	–	–
CH_3D	–	–
CH_2D_2	–	–
CHD_3	–	–
CD_4	40.5	14
C_2D_2	58.5	20
C_2D_4	trace	61
C_2D_6	trace	–

quantitative means of characterization:

$$(CLi_nH_{4-n})_x + D_2O \rightarrow CD_nH_{4-n} + nLiOD$$

We have not seen, in the years we have studied such reactions, spurious results from such careful (~ 2 days) hydrolyses. Derivatization with chlorotrimethylsilane and other species, which has been studied for each of the lithiomethanes, is not so quantitative and is governed often by steric factors.

Discussion

The lithium vapor syntheses involving the chloromethanes have yielded several interesting results. First, in addition to preparing methyllithium, dilithiomethane and tetralithiomethane in good yields, a new polylithium compound, trilithiomethane $(HCLi_3)_n$, was synthesized [13]. Second, several general trends (i.e., the number of lithium substituents, the selective activation of the C–H bond and the number of C_2 lithiated species among the chloromethane reaction products) have been observed. Finally, the problem associated with the lithium metal matrix, which has hampered previous characterization of lithiocarbons produced by the metal vapor technique has been eliminated.

In the production of the lithiomethanes it is observed that the number of lithium substituents parallels the number of C–Cl bonds per chloromethane. This trend is supported by the lithium vapor reactions of CH_3Cl, CH_2Cl_2 and CCl_4 (Table 1). In these reactions an almost total conversion of the chloromethanes to their lithiated analogs, based solely on the lithiomethanes, was observed.

From this observation it appears that the C–Cl bonds became sufficiently activated toward lithium substitution, while the C–H bonds, in the cases of CH_3Cl and CH_2Cl_2, were not as likely to react. For these lithium vapor syntheses, this point is significant. Previous studies done at 800–1000°C have indicated that when dihalo-propanes, -pentanes and -hexanes, in addition to metal-methyl, -ethyl and -halomethyl alkyls were reacted with lithium atoms, predominantly perlithiated alkyl compounds were formed [16,17]. No partially lithiated compounds, except for ethyllithium from the reactions involving tetraethyllead and tetraethyltin, were formed. Furthermore, when CH_2Cl_2 is reacted with lithium vapor at 850°C, the selectivity observed for CH_2Cl_2 reacted with lithium vapor at 750°C is lost. We explain this with more extensive vibrational excitation of carbon–hydrogen bonds thus lowering the activation energy [17].

This reaction at 850°C was performed in conjunction with this study involving the chloromethanes. The results of the CH_2Cl_2 reaction are listed in Table 2. By examining this table, it appears that higher temperatures do promote the lability of hydrogen atoms toward lithium substitution yielding a greater number of polylithium compounds. However, even at 750°C, the lability of the hydrogen atoms toward substitution by a lithium atom showed up significantly when chloroform was used as a substrate (Table 1).

With chloroform as a substrate, the first trend no longer held, and $(CLi_4)_n$, $(HCLi_3)_n$ and $(CH_2Li_2)_n$ were generated in about 30% yield each, based on the production of the lithiomethanes. The replacement of three C–Cl bonds appears to facilitate the lithium substitution of the hydrogen atom, thus forming $(CLi_4)_n$. A more highly hydrogenated product, $(CH_2Li_2)_n$, and a new polylithium compound, $(HCLi_3)_n$, were also synthesized.

As was noted before, previous work has substantiated C–H bond activation due to vibrational excitation from the successive abstraction reactions of chlorine atoms by lithium atoms [17]. Free radicals, having been observed to form from reactions of alkylhalides with lithium atoms, most certainly are implicated in lithium vapor syntheses [17,18]. Cocondensation of lithium atoms with CH_2Cl_2 [19], $CHCl_3$ [20] and CCl_4 [21], as well as CH_3I and CH_3Br [22], have been observed to form the corresponding free radicals in inert matrices.

It is further observed that the greater the number of C–Cl bonds per chloromethane, the greater the yield of C_2 molecules, most notably lithium carbide. This trend is followed throughout all of the chloromethane reactions (Table 1). This trend has been observed in the past [16] and perhaps may be attributed to the increased probability of coupling reactions between two radicals.

As the number of C–Cl bonds increases, the production of free radicals also increases. The greater number of free radicals can account for the increased incidence of a coupling reaction which leads to the subsequent production of a C_2 lithium compound. Note that methyllithium $(CH_3Li)_4$ is formed in 97% yield with few by-products. By contrasting the lithium vapor reactions of CH_2Cl_2 (Table 2) and CCl_4 (Table 3) at different temperatures, it can be seen that milder reaction conditions used in this study have decreased the impact of this trend.

As contrasted in Table 3, reactions of lithium vapor with CCl_4 at 800°C and the milder temperature of 750°C yielded different results from each other. At the milder reaction conditions used in this study, the yield for $(CLi_4)_n$ rose to 41% from 14%, $(C_2Li_2)_n$ rose to 58% and $(C_2Li_4)_n$ decreased to only a trace amount. From a comparison of the CCl_4 reaction at the two conditions, the amount of coupling of free radicals, measured by the overall production of C_2 lithium compounds, decreased from 81 to 58% when milder conditions were used. Also, perhaps the use of milder synthetic conditions accounts for the synthesis of $(HCLi_3)_n$, which before this work had been undertaken had only been theoretically postulated. Furthermore, increasing the reaction temperature from 750 to 850°C, the lithium vapor-CH_2Cl_2 reaction gave a corresponding increase in C_2 lithium compounds from 30 to 42% (Table 2).

Schleyer and Pople have proposed gas phase structures for all of the variously lithium substituted methane monomers [4]. The H–C–H bond angle in methyllithium has been postulated to be 115°. *Cis* and *trans* planar structures have been proposed for dilithiomethane, the *cis* planar structure being more stable. The Li–C–Li bond angle of the *cis* planar structure is proposed to be about 98°. The Li–C–Li bond angles of $(HCLi_3)_n$ are proposed to be about 102° and the Li–C–Li bond angles of $(CLi_4)_n$ at 90°, forming a planar molecule. The increased stabilization of the planar arrangement over the tetrahedral arrangement with increasing lithium substitution is credited to the π-acceptor-σ-donor character of lithium as a substituent [3].

Recently, the stoichiometries of the vapor species of methyllithium [23] and dilithiomethane [9] have been obtained by flash vaporization mass spectrometry. Besides monomers, dimers, trimers and higher polymeric clusters are observed in the mass spectra. Mass spectra of the lithiated methanes reported in this manuscript are given in Tables 4–7. The sample probe and experimental details are described elsewhere [9,23].

TABLE 4

MAJOR IONS FROM THE FLASH VAPORIZATION MASS SPECTRUM OF METHYLLITHIUM $(CH_3Li)_4$

Positive ion	*m/e*	*n*
$(CH_3Li)_n$	$(22)_n$	1–4
$(CH_3Li)_nLi$	$(22)_n + 7$	1–4
$(CH_3)_nLi_{n-1}$	$(22)_n - 7$	2–4

TABLE 5

MAJOR IONS FROM THE FLASH VAPORIZATION MASS SPECTRUM OF DILITHIOMETHANE $(CH_2Li_2)_n$

Positive ion	*m/e*	*n*
$(CH_2Li_2)_n$	$(28)n$	1–4
$(CH_2)_nLi_{2n-1}$	$(28)_n - 7$	2–6
$(CH_2Li_2)_nLi$	$(28)_n + 7$	1–4
$(C_2Li_2)_n$	$(38)_n$	1–3

TABLE 6

MAJOR IONS FROM THE FLASH VAPORIZATION MASS SPECTRUM OF TRILITHIOMETHANE $(CHLi_3)_n$

Positive ion	*m/e*	*n*
$(CH_3Li)_n$	$(22)n$	1–4
$(CH_3Li)_nLi$	$(22)_n + 7$	1–4
$(CH_2Li_2)_n$	$(28)_n$	1–4
$(CH_2Li_2)_nLi$	$(28)_n + 7$	1–4
$(CHLi_3)_n$	$(34)_n$	1–4
$(CHLi_3)_nLi$	$(34)_n + 7$	1–4
$(CLi_4)_n$	$(40)_n$	1–4
$(CLi_4)_nLi$	$(40)_n + 7$	1–4
$(C_2Li_2)_n$	$(38)_n$	1–4
$(CH_3)_nLi_{n-1}$	$(22)_n - 7$	2–6
$(CH_2)_nLi_{2n-1}$	$(28)_n - 7$	1–6
$C_nH_nLi_{3n-1}$	$(34)_n - 7$	1–5
C_nLi_{4n-1}	$(40)_n - 7$	1–4

TABLE 7

MAJOR IONS FROM THE FLASH VAPORIZATION MASS SPECTRUM OF TETRALITHIOMETHANE $(CLi_4)_n$

Positive ion	*m/e*	*n*
$(CLi_4)_n$	$(40)_n$	1–3
$(CLi_2)_nLi_{2n-1}$	$(40)_n - 7$	1–4
$(CLi_4)_nLi$	$(40)_n + 7$	1–4
$(C_2Li_2)_n$	$(38)_n$	1–3
$(C_2Li)_nLi_{n-1}$	$(38)_n - 7$	1–3

The samples were prepared for mass spectral study and purified by grinding the reaction product under argon (extreme care must be taken). The powder was sieved through 100 mesh screens resulting in removal of substantial amounts of lithium metal and approximately 85% pure lithiocarbon product. Subsequently the products are extracted with cold (−20°C) THF to remove LiCl and are then separated from lower density lithium rich particles by flotation on cold THF. Purity of the resulting product ranges as high as 90 to 95%.

In the case of $(CH_3Li)_4$ and $CH_2Li_2)_n$ [9] it is possible to confirm the mass spectra by comparison with samples of higher purity obtained from conventional synthetic methods. To date, $(CLi_4)_n$ and $(CLi_3H)_n$ have been prepared only by these lithium vapor synthetic methods. The mass spectrum of trilithiomethane is complicated by the fact that methods have not yet been developed to separate one lithium substituted methane from a mixture of others. Therefore, although the mass spectrum clearly contains polymers of trilithiomethane, $(CLi_3H)_n{}^+$, assignment of certain fragmentation to specific precursors could be only speculative in view of such impurities. Undoubtedly this is why such a large number of peaks are observed.

The observation of such ions indicates that calculations made on polymeric species to accurately model their electronic states would be valuable.

In light of such observations, Schleyer and Pople have begun focusing more attention to ab initio calculational efforts towards the prediction of the structures and stabilities of dimers and other polymers in the gas phase. Their calculations have indicated that many dimers and trimers are exceedingly stable [5,6].

The lithium vapor-chlorocarbon synthetic method [1] has therefore been adjusted to produce as high a yield of methyllithium as 97.4% based on CH_3Cl, of dilithiomethane as 65.9% based on CH_2Cl_2, of trilithiomethane as 15.5% based on $CHLi_3$ and as high a yield of tetralithiomethane as 40.5% based on CCl_4. Further the only significant by-product in the CCl_4 reaction is lithium acetylide $(C_2Li_2)_n$ which is more easily separated from $(CLi_4)_n$.

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