Some observations on the pyrolysis of methyllithium *

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(Received February 19, 1991; in revised form September 10, 1991)

Abstract

To obtain a more detailed understanding of the synthesis of dilithiomethane by pyrolysis of methyllithium, we have studied this reaction in detail with mixtures of labeled methyllithium precursors. We have also made a detailed study of the gaseous products of the pyrolysis which include several hydrocarbons in addition to methane. This information may be important in establishing a mechanism for the pyrolysis of methyllithium.

Introduction

The structures and properties of dilithiomethane are of much current interest. The solid state structure of dilithiomethane has just been reported [1] and we have recently modified the synthesis such that the same general reaction strategy provides a route to a number of substituted dilithiomethanes [2] including 1,1-di-lithio-2,2,3,3-tetramethylcyclopropane. Originally our group had improved the dilithiomethane synthesis of Ziegler [3] to obtain 99% yields [4]. The structure of the dilithiomethane monomer is also of current interest [5] and has been forecast by Schleyer and Pople [6] to be tetrahedral. The planar form is only a few kcal/mol higher in energy and therefore is a candidate for a matrix isolable planar carbon species as fluxional behavior has been proposed by these workers. The pyrolysis reaction has been generally written

$$(CH_3Li)_4 \rightarrow 2CH_2Li_2 + 2CH_4$$

Results and discussion

We have determined by pyrolysis of mixtures of deuterium-substituted methyllithium and hydrogen-substituted methyllithium that the reaction proceeds by

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* This contribution is dedicated to Professor Erwin Weiss on the occasion of his sixty-fifth birthday.

either an intermolecular process or by a combination of intra- and intermolecular processes. In this study an equal molar mixture of $(CD_3Li)_4$ and $(CH_3Li)_4$ was pyrolyzed at 230°C. This temperature is intermediate between that needed to pyrolyze $(CH_3Li)_4$ (225°C) and the 235°C needed to pyrolyze $(CD_3Li)_4$ [4c]. The gases evolved from the reaction were then analyzed by mass spectroscopy. The results revealed that all of the gases that evolved contained mixed labels (see Table 1). Early in the reaction sequence samples taken from the reaction showed that CH_4 (mass 16) was the predominent gaseous pyrolysis product. As the reaction proceeded, other mixed species were observed at masses 17, 18 and 19. Later in the reaction the predominant species were seen at mass 18 (see Table 1). By hydrolysis of the solid products of the reaction again we obtained evidence for a mixture of labeled and unlabeled dilithiomethane [4]. This analysis was done by mass spectroscopy on both the D_2O and the H_2O derivatives of the solids. The presence of CH_4 in the early stages of the reaction and the increase in labeled species in the latter stages of the reaction was thought to be caused by the difference in the pyrolysis temperatures of the starting materials. Thus only an entirely intramolecular mechanism can be ruled out.

With these results in hand, an attempt to obtain more information about the reaction was undertaken. It is noteworthy that all other pyrolyses of lithium compounds proceed by lithium hydride elimination to produce lithium hydride and alkenes [7]. Therefore we considered the possibility that this pyrolysis also proceeded by a similar mechanism. We had previously shown that lithium hydride is a product in the pyrolysis of methyllithium [4c]. In our mass spectroscopic studies of the gases that evolved from the pyrolysis of methyllithium, besides methane, we determined that a moderate amount of ethylene and smaller amounts of C_3, C_4 and C_5 alkenes were also present along with their respective alkanes. When the gases were analyzed by gas chromatography (see Table 2), it was possible to determine which isomers were present. The C_5 species and the alkanes, other than ethane, were not observed by gas chromatography because they are produced in low yields ($< 0.01\%$). These same products were found when $(CD_3Li)_4$ was pyrolyzed, except that the gaseous products contained deuterium substitution instead of hydrogen substitution. The quantities of the gaseous products follow the general trend that with the addition of another carbon atom to the chain, a decrease in the yield results. This would be expected, if the presence of each successive compound depended first upon the synthesis of the previous one (i.e., the formation of propylene depended on ethylene first being formed). However, isobutene is formed in greater amounts than propylene and allene is found in trace amounts. A possible explanation for this phenomena is that it is more difficult to obtain addition across the double bond in the branched isobutene than for the straight-chain propylene. Therefore, isobutene acts as a cap and end group when lengthening the chain. We believe that because allene is formed in such small quantities that it may be a product of decomposition of dilithiomethane [8*].

These gases were also shown to contain mixtures of hydrogen and deuterium when the mixture of methyllithium isotopes was pyrolyzed together. A possible

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* Reference number with asterisk indicates a note in the list of references.

explanation for these observations would be the following series of reactions:

$$(CH_3Li)_4 \rightleftharpoons 2(CH_3Li)_2 \tag{1}$$

$$2(CH_3Li)_2 \rightarrow 2CH_2Li_2 + 2CH_4 \tag{2}$$

$$(CH_3Li)_2 \rightleftharpoons CH_3CH_2Li + LiH \tag{3}$$

$$CH_3CH_2Li \rightarrow H_2C=CH_2 + LiH \tag{4}$$

$$H_2C=CH_2 + CH_3Li \rightarrow CH_3CH_2CH_2Li \tag{5}$$

$$CH_3CH_2CH_2Li \rightarrow CH_3CH=CH_2 + LiH \tag{6}$$

$$CH_3CH=CH_2 + CH_3Li \rightarrow (CH_3)_2CHCH_2Li \tag{7}$$

$$(CH_3)_2CHCH_2Li \rightarrow (CH_3)_2C=CH_2 + LiH \tag{8}$$

The methyllithium tetramer may or may not break into dimers as in eq. 1. However, this could be a rational course for the reaction. It has previously been shown experimentally [9] and theoretically [10] that the dimer is an intermediate in other processes. The dimer of methyllithium possibly exists as the structure below. Schleyer and coworkers have found this structure to be an energy minimum [11].

$$H_2C \underset{Li}{\overset{Li}{\diamond}} CH_3$$
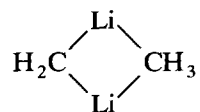
Either the dimeric structure (shown above) or the tetramer could undergo elimination of lithium hydride followed by carbon–carbon bond formation to produce ethyllithium. It is also possible that the intermediates, ethyllithium and propyllithium, react with one another to produce the longer chains. The presence of the 2-butene species could be explained by the addition of ethyllithium to ethylene followed by a loss of lithium hydride. The alkanes that are formed in the reaction might then arise from the metallation of the product olefins by organolithium compounds as has been previously demonstrated [12].

$$CH_3CH_2Li + H_3C-\overset{H}{\underset{|}{C}}=CH_2 \longrightarrow H_3C-\overset{Li}{\underset{|}{C}}=CH_2 + C_2H_6$$
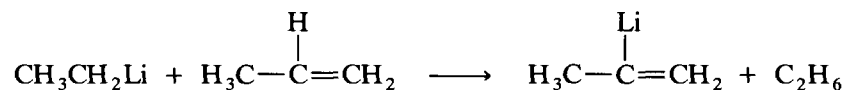
In an additional study, an intimate mixture of methyllithium and ethyllithium was made from ethyllithium and dimethylmercury [13–15]. This mixture was then pyrolyzed at 223–225°C. No noticeable sublimation of ethyllithium was detected if the temperature of the reaction was slowly raised to the pyrolysis temperature. It is probable that ethyllithium does not sublime from the pyrolysis mixture because it is complexed as mixed tetramers with methyllithium. The gases that were produced from the reaction were once again analyzed by mass spectroscopy and gas chromatography. As the reaction proceeded, the gases that evolved were identical to those produced by the pyrolysis of methyllithium, the only difference being in relative yield of products. Less methane was produced in the reaction. With the exception of propylene and isobutylene, all of the other gases were produced in larger quantities than for the pyrolysis of pure methyllithium (see Table 3). An explanation for the production of these two gases in lower yields could be the fact that their formation depends on the amount of methyllithium available to the

Table 1

Yields (%) of labeled methane species [17*]

Species	Minutes									
	15	30	45	60	90	120	150	180	220	240
CH_4	47.2	42.4	37.3	27.3	25.1	23.1	22.2	17.8	21.7	1.3
CH_3D	23.1	24.5	27.4	21.0	22.9	15.7	8.8	0.0	0.5	0.0
CH_2D_2	7.7	12.0	18.3	32.5	33.7	34.7	36.7	50.3	34.2	39.4
CHD_3	15.2	17.4	14.3	15.1	14.0	20.3	23.0	29.2	34.3	55.0
CD_4	6.8	3.7	2.7	4.1	4.2	6.2	9.3	2.8	9.4	4.2

Table 2

GC data from the CH_3Li pyrolysis [18*]

Gases	Yields (%)
Methane	75.19
Ethylene	20.84
Isobutene	2.04
Propylene	1.65
Ethane	0.26
Allene	0.01
trans-2-Butene	Trace

respective alkenes. Therefore, with lower concentrations of methyllithium in early stages, the yields steadily decrease. After about 6 h at this temperature, the pressure of the reaction was returned to the original pressure of 1 mTorr. A sample of the solid was hydrolyzed with D_2O and the gaseous products analyzed by mass spectroscopy. The hydrolysis results showed only CH_2D_2, corresponding to dilithiomethane and HD corresponding to LiH. If the reaction was terminated at an earlier time, some ethyllithium and methyllithium were still present. The production of identical gases indicates that these species may be produced after the interaction of methyllithium and ethyllithium had occurred. The solid product was also analyzed by X-ray powder diffraction and found to match that of CH_2Li_2 [7]. The intensity of the dilithiomethane spectrum decreased as more lithium hydride was formed in this reaction.

We repeated the pyrolysis of the mixture of methyllithium and d_3-methyllithium and found once again mixed protium and deuterium species. This proves that the mixture of the deuterium and protium labeled species had occurred before our proposed step 4 which involves reversible reactions of the methyllithium tetramer to form ethyllithium. Steps 1 and 3 would therefore be reversible as indicated by the appearance of mass 18 (the species for mass 18 methane products). If dilithiomethane were produced by the intermolecular reaction only (without assuming equilibrium), then one would observe only masses 17 and 19 in the methane region corresponding to the exchange of one deuterium and one hydrogen, respectively.

Table 3

GC data from the $CH_3Li/EtLi$ complex pyrolysis [18*]

Gases	Yields (%)
Methane	53.65
Ethylene	34.03
Ethane	8.19
trans-2-Butene	2.08
Isobutene	1.71
Propylene	0.27
Allene	0.08

Experimental

Methyllithium [7], ethyllithium [16], d_3-methyllithium [7] and the ethyllithium/ methyllithium complex [13], were all prepared by transmetallation from the respective organomercury compounds by previously published methods [4a]. Thus there was no halide contamination in the reaction products.

All pyrolyses were carried out under a vacuum in carefully dried glassware. The gases were collected in a liquid nitrogen trap and then transferred to a gas collection tube for analysis by mass spectroscopy. The solid products were then hydrolyzed with D_2O (and/or H_2O). The gaseous derivatives were then collected in a gas collection tube for analysis by mass spectroscopy. Low resolution electron impact mass spectroscopic analyses were carried out on a Bell and Howell 21-491 mass spectrometer with a 70 eV ionization potential. Powder pattern studies were done on a Philips PW 1729 spectrometer.

Gases were analyzed by GC on a 80/100 Hayesep Q 8 ft × 1/8 in column. The temperature of the column was 90°C with a helium pressure of 20 psi. The retention times of the gases were matched with those of pure sample gases. Yields were determined by GC.

Pyrolysis of methyllithium

Typically, 0.1 g of methyllithium was placed in an oven-dried round-bottom flask equipped with a glass encased magnetic stirbar. Teflon-coated stirbars began to decompose at the pyrolysis temperatures and interfered with the disproportionation reaction. The flask was then evacuated. A silicone oil bath was used to slowly heat the reaction to the desired temperature, depending on whether it was (CH_3Li) or (CD_3Li). The flask was then heated until the pressure returned to the starting point. The total reaction time was 8–12 h. The products were derivatized as stated above, and analyzed by mass spectroscopy.

MS data for CH_2Li_2 derivative with D_2O, m/e (%): 16 (27.83), 17 (53.46), 18 (100), 19 (6.49), 20 (1.34). MS data for CD_2Li_2 derivative with D_2O, m/e (%): 16 (20.21), 17 (19.72), 18 (88.47), 19 (36.11), 20 (100). MS data for CD_2Li_2 derivative with H_2O, m/e (%): 16 (25.37), 17 (54.36), 18 (100), 19 (5.21), 20 (1.07).

Pyrolysis of $(CH_3Li)/(CD_3Li)$ mixture

Typically, 0.025 g (1 mmol) of $(CH_3Li)_4$ and 0.028 g (1 mmol) of $(CD_3Li)_4$ were combined as solids and stirred to insure complete mixing. The reaction was then carried out as stated above for methyllithium. The temperature of the oil bath was maintained between 230 and 232°C while samples of the gaseous products were collected every 15 min for the first hour and then every 30 min for the next 5 h. See Table 1 for the gaseous product results from this reaction.

The solid was derivatized with D_2O, and the products analyzed by mass spectroscopy. D_2O derivatized results, m/e (%): 16 (78.97), 17 (100), 18 (95.69), 19 (11.72), 20 (81.21). A later sampling: 16 (65.28), 17 (45.45), 18 (100), 19 (61.12), 20 (1.31).

Pyrolysis of the ethyllithium/methyllithium complex

Typically, 0.1 g of the complex was pyrolyzed using the same procedures. The temperature needed to be raised more slowly than for the pyrolysis of methyl-

lithium to prevent sublimation of ethyllithium. The pyrolysis gases were collected every 15 min for the first hour and every 30 min for the remainder of the reaction. After 6 h at 225°C, the oil bath was removed and the reaction products were analyzed as before.

MS data for derivatized products, with D_2O, (methane region) m/e (%): 16 (48.23), 17 (80.06), 18 (100), 19 (5.13), 20 (1.02).

Acknowledgments

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18 Tables 2 and 3 do not include yields for the alkanes (other than ethane) and the C_5 species, since they did not register on the gas chromatograph.