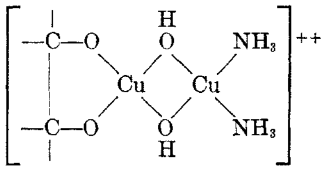
cyclohexanediols with cuprammonium reagent, more nearly approach the theoretical curves.

A remote possibility is that another (soluble) copper-containing compound (not involving a diol) is formed simultaneously with the copper-diol complex. Should this occur, the copper–diol ratio in the complex could be 1:1.

The structure of a probable cuprammonium–diol complex having a copper–diol ratio of 2:1 is as follows. Coordination compounds of copper are planar; thus, the ammonia groups must be located at the four corners of a square, with the copper atom in the middle. A possible interpretation is that a binuclear complex of the form



exists in the strongly ammoniacal solution. Occurrence of such a reaction would account for (a) the decrease in conductivity that accompanies formation of the copper–diol complex and (b) the 2:1 copper–diol ratio.

EXPERIMENTAL

The cuprammonium reagent was prepared, and analyzed for copper and ammonia, according to the procedure described by TAPPI.[15] Each diol was dissolved in concentrated ammonia water in which the ammonia concentration was the same as that in the cuprammonium reagent. An appropriate amount of the cuprammonium reagent and of the respective diol solution were placed in a 10-ml. flask, and the solution was made up to 10 ml. with concentrated ammonia water. All solutions were kept in an ice bath until each reaction mixture had been brought to final volume. Each was then transferred to a capped vial and allowed to warm up to room temperature. Ammonia analyses on a series of sucrose–cuprammonium reaction mixtures showed that a uniform ammonia concentration was still present after 24 hr. Absorption observations were made with a Beckman spectrophotometer at room temperature; cell depths of 0.4 cm. were used. In all experiments, the absorption values of the blanks, which contained the cuprammonium reagent plus ammonium hydroxide, were found to follow Beer's law. The experimental points shown in Figs. 1–4 were obtained by subtracting the absorption of the blank cuprammonium solution from that of the reaction mixture at each concentration.

cis-1,2-Cyclohexanediol was prepared by oxidation of cyclohexene with permanganate, according to the procedure of Clarke and Owen,[16] m.p. 98°. *trans*-1,2-Cyclohexanediol was prepared by oxidation of cyclohexene with performic acid, as described by Roebuck and Adkins,[17] m.p. 104–105°.

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[15] Recommended Practices of the Technical Association of the Pulp and Paper Industry, T 206 m-55.

[16] M. Clarke and L. Owen, *J. Chem. Soc.*, 318 (1949).

[17] A. Roebuck and H. Adkins, *Org. Syntheses*, **28**, 35 (1948).

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF LITHIUM CORP. OF AMERICA]

Analysis and Stability of *n*-Butyllithium Solutions in *n*-Heptane

CONRAD W. KAMIENSKI AND DONALD L. ESMAY

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The purity of the ether has been shown to have a marked effect when the "double titration" procedure is used in analyzing solutions for n-butyllithium content. Results of these studies show that a reasonably accurate determination of the n-butyllithium content in n-heptane solutions is obtained by a single, direct acid titration of a hydrolyzed sample of the solution. Determination of the n-butyl chloride content by use of the disodium biphenyl reagent has been shown to be suitable for direct analysis of n-butyllithium solutions in n-heptane. Essentially no change in n-butyllithium content occurred on storing n-heptane solutions at room temperature for over three months. The density at 26° of a 2.59 molar solution of n-butyllithium in n-heptane was found to be 0.697 ± 0.001.

The analysis and stability of organolithium solutions have been of continuing interest for many years. Stability studies have been complicated by the necessity of determining the amount of an organolithium compound present in the presence of compounds formed during its deterioration. Any one of several methods can be used for such an analysis with varying degrees of accuracy and convenience. The "double titration" or "indirect titration" procedure developed by Gilman and Haubein[1] probably has been used the most widely. This procedure involves hydrolyzing directly one sample of the organolithium solution followed by acid titration to determine the total base present. A second sample is treated with benzyl chloride then hydrolyzed and titrated with acid. As most organolithium, particularly, alkyllithium, compounds react rapidly with benzyl chloride to form non-alkaline products, this titration determines the residual alkalinity due to materials originally present which did not contain carbon-lithium bonds. The difference between the total alkalinity and the residual alkalinity should provide an accurate measure of the amount of organolithium compound present. Certain difficulties encountered in obtain-

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

TABLE I

VARIATION OF RESIDUAL ALKALINITY WITH VARYING REACTION CONDITIONS

Run No.	Solvent for n-Butyllithium	Normality of n-Butyllithium Solution	Vol. of Aliquot, Ml.	Solvent[a] for Reaction with Benzyl Chloride, Ml.	Benzyl Chloride, Ml.	Alk. Titer of[b] Benzyl Chloride Reaction Mixture, Meq./Ml.	Description of Reaction Mixture
1	n-Heptane	1.96	1	n-Heptane, 10	1	1.42	No ppt.[c]
2	n-Heptane	1.96	1	Ether, 30	1	0.764	Ppt.[c,d]
3	n-Heptane	1.96	1	Ether, 50	2 (R.A.)[e]	1.85	Slight ppt.[f,g]
4	n-Heptane	1.96	1	n-Heptane, 10	2 (R.A.)	1.38	No ppt.[c]
5	Anhyd. Et_2O	0.50	5	Ether, 10	1	0.31	Ppt.[c,d]
6	Anhyd. Et_2O	1.29	5	Ether, 10	2	0.20	Ppt.[c,d]
7	Anhyd. Et_2O	1.29	5	Ether, 10	2 ϕ-CH_2Br	0.19	No ppt.[c,d]
8	Anhyd. Et_2O	1.00	5	Ether, 10	1	0.23	Ppt.[c,d]
9	Anhyd. Et_2O	1.00	5	Ether, 10	2	0.22	Ppt.[c,d]
10	Anhyd. Et_2O	1.00	10	Ether, 10	3	0.16	Ppt.[c,d]

[a] The n-heptane was Phillips Pure Grade (99 mol.%) which had been dried over sodium ribbon. The ether was Mallinckrodt Anhydrous Grade which had been shaken with lithium hydride and stored several months over the same reagent. [b] Color test I negative before hydrolysis. [c] Heat evolved. [d] Yellow color. [e] (R.A.) = reverse addition. [f] No heat evolved. [g] No color formed.

ing consistent results by the "double titration" method were recently reported[2] which parallel in some respects observations in our laboratories. This prompts us to report the results of certain analytical and associated experiments carried out during a thorough study of the preparation of n-butyllithium.

The data given in Table I are an indication of some of the inconsistent results which we obtained with the "double titration" procedure during our early studies. For example, the first four runs listed show that rather minor changes in the analytical procedure had gross effects on the answers obtained. The results of Runs 6 and 7 confirmed an early conclusion that the difficulties encountered were not necessarily associated with the benzyl chloride being used since essentially identical results were obtained using benzyl bromide in place of the benzyl chloride.

Review of a large number of data, such as given in Table I, indicated that the use of impure ether could be the cause of the erratic results. The results given in Table II provided confirming evidence of this concept in that increasing the amount of ether used in the "double titration" apparently increased the amount of non-butyllithium alkaline material in the sample. This could be explained by assuming that the ether contained a limited amount of impurity, for example, water, which reacted with the n-butyllithium. Extrapolation of the results given in Table II indicated that sufficient impurity should be present in 100 ml. of the ether to destroy all of the n-butyllithium in a 1-ml. aliquot. This proved to be essentially correct.

TABLE II

VARIATION OF RESIDUAL ALKALINITY WITH VARYING AMOUNTS OF SLIGHTLY IMPURE ETHER[a]

Ether,[b] Ml.	Acid Used in Titration, Ml.	Base in Sample, Meq.
5	0.65[c]	0.33
7.5	0.72	0.36
10	1.08[c]	0.54
15	1.21[c]	0.61
20	1.47[c]	0.74
25	1.87[c]	0.94
30	2.34	1.18

[a] Constants: Normality of n-heptane solution of n-butyllithium = 1.97. Volume of aliquot used = 1.0 ml. Volume of benzyl chloride used = 1.0 ml. [b] The ether was Mallinckrodt Anhydrous Grade which had been shaken with lithium hydride and then stored over it for several months. [c] Average of two values.

TABLE III

VARIATION OF RESIDUAL ALKALINITY WITH THE SIZE OF THE ALIQUOT USING SLIGHTLY IMPURE ETHER

Aliquot,[a] Ml.	Total Base in Aliquot, Meq.	Benzyl Chloride, Ml.	Ether,[b] Ml.	Acid Used in Titration, Ml.	Base in Blank, Meq.	% Total Base in Blank
1	2	0.5	20	1.88	0.94	47
2	4	1.0	20	2.04[c]	1.02	26
3	6	2.0	20	2.09	1.05	18
5	10	2.5	20	2.49	1.25	13
10	20	5.0	20	3.15	1.58	8

[a] Aliquots were taken from the same n-butyllithium solution described in Table II. [b] The ether was Mallinckrodt Anhydrous Grade which had been shaken with lithium hydride and stored over it for several months. [c] Average of two values.

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(2) A. F. Clifford and R. R. Olsen, Papers presented at the 135th Meeting of the American Chemical Society, Boston, Mass., April 5–10, 1959.

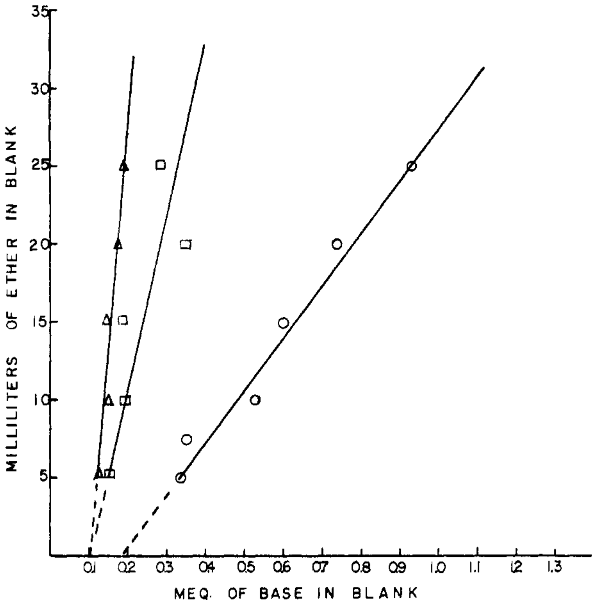

Fig. 1. Variation of residual alkalinity with varying methods of purifying the ether solvent. See Tables II and IV

△ Ether dried by lithium aluminum hydride
□ Sodium-dried ether
○ Ether dried by lithium hydride

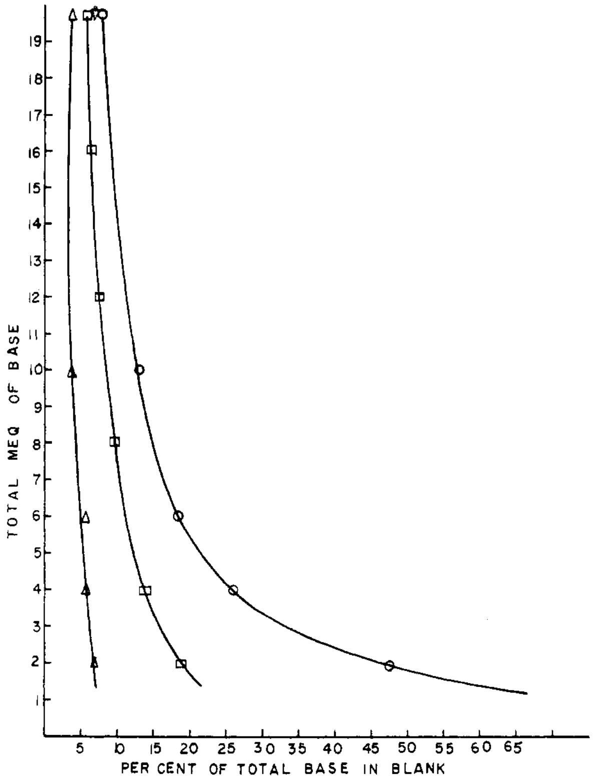

Fig. 2. Variation of residual alkalinity with variation in the size of the n-butyllithium aliquot using ether purified in various ways. See Tables III and V

△ Ether dried by lithium aluminum hydride
□ Sodium-dried ether
○ Ether dried by lithium hydride

The results shown in Table III provided further evidence that slightly impure ether was the cause of our trouble. As the size of the n-butyllithium aliquot was increased, there was a regular decrease in the per cent of the total base found in the benzyl chloride "blank."

The data given in Tables IV and V show that use of rigorously purified ether essentially eliminated the variations reported in Tables II and III. The ether was purified by refluxing over and then distilling from lithium aluminum hydride into carefully dried storage containers. In order to emphasize the above results, selected data from Tables II and IV and from Tables III and V are shown graphically in Figs. 1 and 2, respectively. Included are some results from similar tests using ether freshly purified over sodium wire. Although the sodium-dried ether gave results that were better than those obtained with the ether which had been stored several months over lithium hydride, the best results were obtained with the ether rigorously purified with lithium aluminum hydride. It is quite possible, of course, that distillation from sodium or lithium hydride, or that use of some other purifying method will give an ether solvent of equivalent purity.

The data given in Tables VI and VII, and graphically presented in Fig. 3, show that consistent

TABLE IV

VARIATION OF RESIDUAL ALKALINITY WITH VARYING AMOUNTS OF PURIFIED ETHER[a]

Ether,[b] Ml.	Acid Used in Titration, Ml.	Base in Blank, Meq.
5	0.23	0.115
10	0.30	0.150
15	0.30	0.150
20	0.34	0.170
25	0.38	0.190

[a] Same constants used as in Table II. [b] The ether was Mallinckrodt Anhydrous Grade which had been refluxed over $LiAlH_4$ for 3 hr. and distilled from this reagent into thoroughly dried glass-stoppered bottles.

TABLE V

VARIATION OF RESIDUAL ALKALINITY WITH THE SIZE OF THE ALIQUOT USING PURIFIED ETHER

Aliquot,[a] Ml.	Total Base in Aliquot, Meq.	Benzyl Chloride, Ml.	Ether,[b] Ml.	Acid Used in Titration, Ml.	Base in Blank, Meq.	% Total Base in Blank
1	2	0.5	20	0.28	0.14	7.0
2	4	1.0	20	0.45	0.225	5.6
3	6	2.0	20	0.69	0.345	5.7
5	10	2.5	20	0.83	0.415	4.1
10	20	5.0	20	1.60	0.80	4.0

[a] Aliquots were taken from the same n-butyllithium solution described in Table II. [b] The ether was Mallinckrodt Anhydrous Grade which had been refluxed over $LiAlH_4$ for 3 hr. and distilled from this reagent into thoroughly dried glass-stoppered bottles.

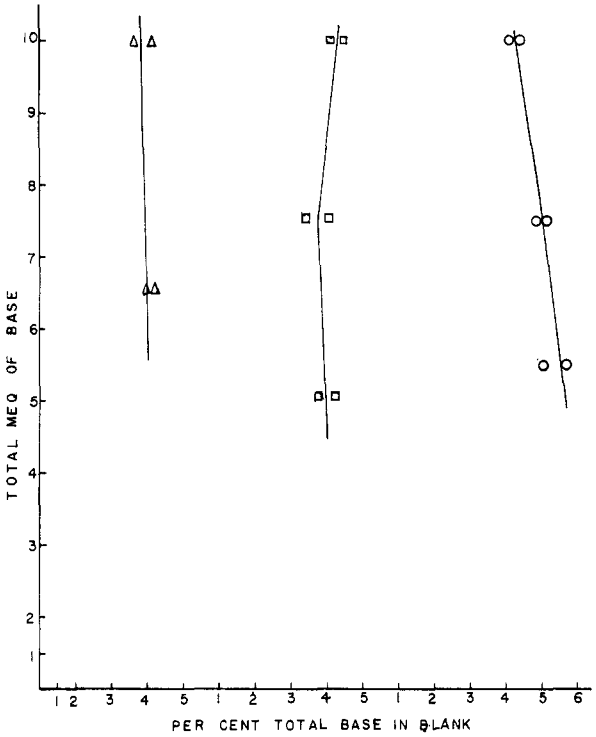

Fig. 3. Variation of residual alkalinity with various concentrations of *n*-butyllithium in *n*-heptane using ether dried by lithium aluminum hydride. See Table VI

△ 3.31 molar *n*-butyllithium soln.
□ 2.51 molar *n*-butyllithium soln.
○ 1.96 molar *n*-butyllithium soln.

TABLE VI

Variation of Residual Alkalinity with Varying Concentrations of *n*-Butyllithium in *n*-Heptane Using Purified Ether

Normality of *n*-BuLi Soln. (in *n*-Heptane)	Aliquot,[a] Ml.	Benzyl Chloride, Ml.	Ether,[b] Ml.	Base Titrated, Meq.	% Total Base in Blank
3.31	2	2.2	10	0.255	3.8
	2	2.2	10	0.273	4.1
	3	3.3	10	0.368	3.7
	3	3.3	10	0.390	3.9
1.96	3	2.0	10	0.310	5.3
	3	2.0	10	0.333	5.7
	4	2.3	10	0.400	5.1
	4	2.3	10	0.380	4.8
	5	2.5	10	0.425	4.3
	5	2.5	10	0.423	4.3
2.51	2	1.7	10	0.208	4.1
	2	1.7	10	0.198	3.9
	3	2.5	10	0.265	3.5
	3	2.5	10	0.298	4.0
	4	3.3	10	0.423	4.2
	4	3.3	10	0.420	4.2

[a] The range of the final concentration of *n*-butyllithium in ether was adjusted, by varying the size of the aliquots, in such a manner as to give a range of from 5 meq./10 ml. of ether to 10 meq./10 ml. of ether. [b] The ether was Mallinckrodt Anhydrous Grade which had been refluxed over $LiAlH_4$ for 3 hr. and distilled from this reagent into thoroughly dried glass-stoppered bottles.

TABLE VII

Summary of Results of Table VI

Normality of *n*-BuLi	Average % of Total Base in Blank	Average Deviation from Average	% Average Deviation from Average
3.31	3.9	0.13	3.2
1.96	4.9	0.45	9
2.51	4.0	0.2	5

results were obtained using the "double titration" analytical procedure for analyzing solutions of *n*-butyllithium in *n*-heptane of various concentrations when rigorously purified ether was used. Further, and of considerable importance, these results show that a direct acid titration of a hydrolyzed sample of *n*-butyllithium in *n*-heptane determines the amount of *n*-butyllithium present with less than 5% error. Conceivably the accuracy of a direct titration may be even better than this as the essentially constant blank of 4 to 5% may be inherent to the "double titration" procedure under the conditions used. These results confirmed our early assumption that essentially no basic lithium-containing materials other than *n*-butyllithium should be present in the *n*-heptane solutions because of the insolubility of such substances in *n*-heptane. Additional confirming evidence was obtained by the preparation of the derivative triphenyl-*n*-butylsilane in essentially quantitative yield.

Having shown that the *n*-heptane solutions contained essentially no basic materials other than *n*-butyllithium, it next became of interest to determine whether any inert materials were present for example, unreacted *n*-butyl chloride or olefins formed by thermal decomposition. Direct analysis of the *n*-heptane solution of *n*-butyllithium by use of the disodium biphenyl reagent[3] was found to be a dependable method for determining *n*-butyl chloride content. It was interesting to note that less than 2% of the starting *n*-butyl chloride remained in those solutions of *n*-butyllithium in *n*-heptane obtained in runs where the yields of *n*-butyllithium based on *n*-butyl chloride ranged above 70%. Since these yields of *n*-butyllithium were less than theoretical, loss of *n*-butyl chloride to some side reaction(s) was indicated. Incomplete studies now in progress using gas chromatography indicate that the amount of *n*-octane in the *n*-heptane solvent increases by an amount approximately equal to the amount of *n*-butyl chloride lost. Thus, it appears that some portion of the *n*-butyl chloride couples with the *n*-butyllithium as it is being formed.

The analyses for unsaturated materials showed that essentially no olefins were formed during the *n*-butyllithium preparations. These results provided

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(3) L. M. Liggett, *Anal. Chem.*, 26, 748 (1948).

evidence that *n*-butyllithium was quite stable at or slightly above room temperature. Additional evidence for this stability was obtained from the shelf-life tests. The results showed that the *n*-butyllithium concentration in *n*-heptane solution remained essentially unchanged for at least 3 months when stored at room temperature in properly sealed containers. The latter is necessary because of the rapid reaction of the *n*-butyllithium solutions with air and water. It was interesting to find from the pyrophoricity studies, however, that these reactions of themselves did not cause ignition of the solution.

EXPERIMENTAL[4]

n-Butyllithium concentration in n-heptane by indirect (double) titration. The procedures followed in these analyses were essentially those given by Gilman and Haubein.[1] Variations and results are given in Tables I through VII. Selected data from the various Tables are shown graphically in Figs. 1 through 3.

n-Butyl chloride concentration in n-heptane solutions of n-butyllithium. (A) *Direct analysis with the disodium biphenyl reagent.* The procedure followed was essentially that of Liggett[3] with certain modifications. A 15-ml. aliquot of an approximately 2.5 molar solution of *n*-butyllithium in *n*-heptane was pipetted into a 250-ml. separatory funnel (previously flushed with argon) containing 50 ml. of dry *n*-heptane (Phillips Pure) and the solution shaken to insure thorough mixing. Twenty ml. of the disodium biphenyl reagent[3] was then pipetted into the separatory funnel and the mixture shaken for 1 to 2 min. with the funnel being inverted and carefully vented at frequent intervals. Persistence of a dark green color indicated the presence of excess disodium biphenyl reagent. The mixture was then extracted with 25 ml. of distilled water, being sure to agitate cautiously until the excess reagent was destroyed (disappearance of color). The lower aqueous layer was drawn off and the upper layer extracted twice with 3*N* nitric acid. The main aqueous layer and extracts were then diluted to 100 ml. in a volumetric flask and titrated with standard silver nitrate solution by the Mohr method.

Weighed amounts of *n*-butyl chloride have been added to control samples of *n*-butyllithium and chloride values with 1–2% accuracy obtained by this method.

(B) *Direct analysis by gas chromatography.* It is entirely possible that *n*-butyl chloride could be determined quantitatively by gas chromatography in the presence of solvents other than *n*-heptane. This solvent, however, appears to mask the presence of *n*-butyl chloride due to the closeness of the relative positions of their peaks. Further work on this method of analysis remains to be done.

(C) *Indirect analysis by determination of by-product lithium chloride.* An estimate of the amount of *n*-butyl chloride remaining in a solution of *n*-butyllithium has been indirectly determined by analysis of the solid, reaction residue isolated after removal of the product solution by filtration. This residue was decomposed by slowly adding it, as a slurry in *n*-heptane, to a large excess of methanol (chloride-free). The resulting mixture was diluted with distilled water, and the aqueous layer separated and acidified carefully with reagent grade dilute nitric acid. The solution was filtered to remove suspended material and the methanol and *n*-heptane azeotroped out. The remaining aqueous solution was diluted to the mark in a volumetric flask and analyzed for chloride ion by the Mohr titration procedure.

Use of methods (A) and (C) has shown that in those *n*-butyllithium preparations performed in this laboratory where the yields ranged above 70%, the amount of unreacted *n*-butyl chloride in 2.0 to 2.5 molar solutions was always less than 1% of the solution.

Olefin concentration in n-heptane solutions of n-butyllithium. (A) *Olefin formed during reaction.* A run of *n*-butyllithium in *n*-heptane (2.5 molar) was made at 35° yielding 1395 g. of solution. During this run the gases were led off through a length of glass tubing running from the reaction flask into a 250-ml., 3 necked flask containing 50 ml. of chloroform and immersed in a Dry Ice–acetone bath. After the run was over, the chloroform solution was titrated with a solution of 4 g. of bromine in 99 g. of glacial acetic acid immediately after removing from the cooling bath. The sample took 16.5 ml. of the bromine solution to produce a permanent yellow color in the solution.

Calculations: 1 ml. of bromine solution was equivalent to 0.25 millimole of monoolefin.

$$16.5 \text{ ml.} \times 0.25 \text{ mmole} = 4.1 \text{ mmole of monoolefin}$$

This amount of monoolefin was formed from 6.25 mol. of *n*-butyl chloride and is equivalent to a 0.06% yield based on *n*-butyl chloride. Based on the 1395 g. of solution and expressed as butene-1, the percentage of unsaturates was less than 0.1%.

(B) *Olefins present in the final product solution.* A 25-ml. sample of a 3.5 molar *n*-butyllithium solution was added dropwise to 100 ml. of distilled water with stirring. The evolved gases were passed into 50 ml. of chloroform contained in a receiver cooled to −78° by a Dry Ice–acetone bath. After the addition was completed, the water-heptane mixture was heated to 55–60° to insure removal of all evolved gases from the reaction vessel. The chloroform solution was then titrated with a bromine solution (see A). The sample took 1 ml. of the bromine solution to produce a permanent yellow color in the solution.

Calculations: 1 ml. of the bromine solution was equivalent to 0.25 millimole of monoolefin. Based on the sample weight of 17.75 g. and expressed as butene-1, the percentage of unsaturates was 0.08%. (The *n*-heptane initially contained 0.04–0.1% unsaturates.)

Triphenyl-n-butylsilane. The procedure followed in this preparation was essentially that given by Gilman, Benkeser, and Dunn.[5] The triphenylchlorosilane (Dow Corning purified grade, m.p. 90–95°) was further purified by distillation at reduced pressure and recrystallization from an anhydrous ethyl ether–petroleum ether (b.p. 60–71°) mixture (1:10). The melting point of this material was 97–99°.

A 25-ml. aliquot of a 2.38 molar *n*-butyllithium solution in *n*-heptane (0.06 mol.) was added dropwise during 15 min. to a stirred solution of 17.8 g. (0.06 mol.) of purified triphenylchlorosilane in 85 ml. of purified diethyl ether (Mallinckrodt anhydrous grade distilled from lithium aluminum hydride). After stirring for 30 min., the mixture was hydrolyzed with 50 ml. of water, the layers were separated, and the ether-heptane layer was dried over anhydrous calcium chloride. On evaporation to dryness, 19.00 g. (quantitative yield) of crude *n*-butyl-triphenylsilane, m.p. 82–88°, was obtained. This was recrystallized from 300 ml. of absolute methyl alcohol to yield 15.75 g. of pure triphenyl-*n*-butylsilane, m.p. 87.5–89° (lit.[5] m.p., 87.5–88.5°). A second crop of 1.21 g. of product was recovered, m.p. 86–87.5°. The combined yield of product to this point was 16.96 g. (89.5%). A third impure crop weighing 0.66 g. was also obtained, m.p. 80–86°.

Density of an n-butyllithium solution in n-heptane. A 10 ± 0.02-ml. aliquot of a solution of *n*-butyllithium in *n*-heptane, 2.59 molar in *n*-butyllithium (as determined by direct titration), was transferred to a tared weighing bottle (previously flushed with argon). The sample weighed 6.956

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[4] All *n*-butyllithium solutions used in these studies had been filtered through a Pall Corporation stainless steel filter. All melting points are uncorrected.

[5] H. Gilman, R. A. Benkeser, and G. E. Dunn, *J. Am. Chem. Soc.*, **72**, 1690 (1950).

g. The ambient temperature was 26°. The *n*-butyllithium solution contained, in addition to *n*-butyllithium, 2.8% heavy mineral oil and less than 9% *n*-octane. Thus, the density of this solution at 26° was 0.697 ± 0.001.

Shelf-life of n-butyllithium solutions in n-heptane. Two solutions of *n*-butyllithium in *n*-heptane were prepared and placed in screw-topped cans (sealed with electrical tape) for shelf-life tests. Can No. 1 (1 quart capacity) contained 340 ml. of 0.639 molar *n*-butyllithium solution, while can No. 2 (1 gallon capacity) contained 1750 ml. of 2.05 molar *n*-butyllithium solution. The data given in Table VIII indicate stability as determined by periodic removal of aliquots from each of the cans (under argon) and analysis of these by hydrolysis and titration with standard acid.

TABLE VIII

RESULTS OF STABILITY TESTS

Can No.	Date of Analysis	Size of Aliquot Taken, Ml.	Concentration of Solution, Molarity	% Change in Molarity from Date of Preparation
1	2/26/58[a]	5	0.639	0
	3/19/58[b]	5	0.620	−3.1
	4/10/58	2	0.615	−3.8
2	3/13/58[a]	2	2.050	0
	4/3/58	2	2.075	+1.2
	6/9/58	2	2.069	+0.9

[a] Date of preparation of these solutions. [b] Screw cap tightened as much as possible and resealed with fresh electrical tape after this aliquot was taken. The old electrical tape had been extensively attacked by the solvent.

Pyrophoricity of n-butyllithium solutions in n-heptane. (A) *Small scale.* A small amount (approx. 1 ml.) of 2 molar *n*-butyllithium in *n*-heptane was placed on a 2-inch-diameter watch glass and allowed to evaporate to dryness. The dry sample did not ignite spontaneously, but formed a white crust. This crust did not react vigorously with water. Another 1-ml. portion of the *n*-heptane solution was placed on a watch glass and a few drops of water added to it. Heat was evolved with some fuming and loss of solvent, but no ignition of the material occurred.

(B) *Large scale.* Two 25-ml. portions of the 2-molar *n*-butyllithium solution were placed in 600-ml. beakers. After standing for 10 minutes, 10 drops of water was added to one of the beakers and 25 ml. of water to the other. A hard white crust formed in both cases with accompanying vigorous frothing in the latter case. In neither case was there spontaneous ignition.

MINNEAPOLIS, MINN.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Effect of Triethylamine on the Decomposition of Amylsodium[1]

AVERY A. MORTON AND FRANK K. WARD

Received August 4, 1958

The decomposition of amylsodium appears to be more a cascade of metalations, eliminations of sodium hydride and polymerization than a splitting into simple fragments. Triethylamine hastens these changes but is not itself metalated or cleaved.

Previous work[2] showed that certain halide salts and alkoxides accelerated the decomposition of amylsodium. Presumably these salts were associated or coordinated with the organosodium salt. The present paper reports that triethylamine, a strong coordinating agent, accelerates the decomposition of amylsodium without being metalated or cleaved itself. To a large extent, however, this decomposition (and probably the previous ones[2] also) was largely a metalation of pentene and other unsaturated hydrocarbon units, accompanied by elimination of sodium hydride and polymerization. So much do these secondary processes prevail that any study of the primary dissociation of the organosodium salt into simple fragments is difficult.

$$C_5H_{11}Cl + 2Na \longrightarrow C_5H_{11}Na + NaCl \qquad (1)$$

The decomposition of amylsodium, prepared by equation 1, was observed at room temperature during 2 years and at 0°, 50° and 80° for shorter times, mostly 3 hr. and not exceeding 10 hr. For analysis, a preparation or an aliquot thereof was carbonated. Thereby sodium hydride became sodium formate. This action was quantitative when very small quantities were used, but this fact was not known until later stages of the work. Consequently the data for formic acid and sodium hydroxide in the tables are not complete. Amylsodium was also converted to sodium caproate and sodium butylmalonate, the latter by a secondary reaction[3,4] which was difficult to suppress, even at −72°, because the thickness of the reaction mixture prevented good contact with carbon dioxide. Pentenylsodium became a mixture of sodium hexenoates. In addition, there was formed the sodium salt of a tarry carboxylic acid, the ultimate analysis of which approached one carboxyl group for each five carbon atoms and approximately five hydrogen atoms. Metallic sodium did not react

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(2) A. A. Morton and E. F. Cluff, *J. Am. Chem. Soc.*, **75**, 134 (1953).

(3) A. A. Morton, J. B. Davidson, and H. A. Newey, *J. Am. Chem. Soc.*, **64**, 2240 (1942).

(4) H. Gilman and H. A. Pacewitz, *J. Am. Chem. Soc.*, **62**, 1301 (1940).