formamidine acetate in 500 ml. of ethanol was heated under reflux for 20 hr. The product gradually separated from the hot reaction mixture in the form of colorless, fluffy plates. The chilled mixture was filtered to yield 4.0 g. of 7-methyladenine-3-*N*-oxide, while concentration of the filtrate yielded an additional 1.5 g.; total yield, 5.5 g. (92%). Recrystallization from ethanol yielded colorless needles, m.p. 278° dec. The product was extremely hygroscopic and was rapidly converted to a monohydrate upon exposure to air.

Anal. Calcd. for $C_6H_7N_5O \cdot H_2O$: C, 39.3; H, 4.95; N, 38.2. Found: C, 39.0; H, 4.8; N, 38.3.

Careful drying just prior to analysis resulted in the loss of 10.1% of the weight of the monohydrate (calculated loss: 9.9%):

Anal. Calcd. for $C_6H_7N_5O$: C, 43.6; H, 4.3; N, 42.4. Found: C, 43.7; H, 4.2; N, 42.5.

$$\lambda_{\max}^{0.1\,N\ \mathrm{NaOH}}\,229,\ 296\ \mathrm{m}\mu;\ \log\epsilon\ 4.23,\ 4.07$$

$$\lambda_{\max}^{0.1\,N\ \mathrm{HCl}}\,224.5,\ 278\ \mathrm{m}\mu;\ \log\epsilon\ 4.06,\ 4.12$$

Reduction of 7-Methyladenine-3-N-oxide to 7-Methyladenine (V). A solution of 1.0 g. of 7-methyladenine-3-*N*-oxide in 80 ml. of water containing 1 ml. of concentrated ammonium hydroxide was hydrogenated in the presence of 1 g. of freshly prepared Raney nickel catalyst (wet with ethanol) at 3 atmospheres pressure and at room temperature for 20 hr. The catalyst was removed by filtration and the filtrate was evaporated to dryness under reduced pressure. Recrystallization of the residue from aqueous ethanol yielded 0.85 g. of 7-methyladenine, m.p. 345°, identical in every respect with an authentic sample.[3]

Acknowledgment. The authors are indebted to Joseph E. Loeffler for stimulating discussions during the course of this work.

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Effect of Sodium in the Preparation of *n*-Butyllithium

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Received June 19, 1959

n-Butyllithium is routinely prepared in this laboratory from 1-bromobutane and lithium metal in diethyl ether by the method of Gilman *et al.*,[1] in yields of 80–95%. Recently metallic lithium of higher grade was made commercially available[2] so it was of interest to determine the effect of this metal on the yield of *n*-butyllithium. According to information supplied by the manufacturer, the main difference between this new lithium metal and the regular grade lithium is the sodium content, which is approximately 0.005% for the new metal compared to 0.05% for the regular grade metal. By following the usual procedure[1] we obtained a maximum yield of only 48% with the "low sodium" lithium compared to 80–95% for the regular grade lithium. Moreover the reaction differs in that a precipitate forms during the reaction, the lithium does not become shiny but turns a dull brownish color, and the temperature fluctuates and is difficult to control.

Reaction conditions have been varied in order to improve the yield. Small pieces of sodium were added with no significant result. The temperature was varied from the usual −30 to −40° to the reflux temperature of the ether. Somewhat better yields were obtained at the higher temperatures with a maximum of 59% at 10°. Special stirrers were designed in an effort to minimize the coating of the lithium, but these were unsuccessful. An increase in addition time of 1-bromobutane from the usual 30 min. to 3 hr. at −35° resulted in a yield of 29%. However, the use of half "low sodium" lithium and half regular grade lithium using routine procedures increased the yield to 76%. In another experiment some of the "low sodium" lithium was melted under oil and approximately 0.1% sodium was added. This metal also gave *n*-butyllithium in 76% yield. "Low sodium" lithium[3] to which 0.8% sodium was added resulted in an 84.2% yield of *n*-butyllithium by conventional procedures.

In the literature are reports of good yields of *n*-butyllithium from 1-chlorobutane and lithium metal in benzene.[4] This reaction was attempted in the conventional way with regular grade lithium metal and resulted in low yields of *n*-butyllithium (32–57%). Since the lithium appeared to be heavily coated, more vigorous stirring was used but this did not improve the yield even though the metal was finely dispersed by the stirrer. The use of a lithium dispersion also did not improve the yield. However, when "low sodium" lithium to which 0.8% sodium was added was used, the yields by the conventional method were increased to 70–80%.

In *n*-heptane "low sodium" lithium and 1-chlorobutane resulted in yields from 71.9–73.7%. Regular lithium gave yields from 64–69.6%, but again "low sodium" lithium, to which 0.8% sodium was added,[3] gave higher yields of 79.2–81.3% by conventional methods.

Apparently the amount of sodium in the lithium metal appreciably affects the yield of *n*-butyllithium[5] from *n*-butyl halides and lithium metal, though the reason for this effect is not clear. The

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(1) H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn, and L. S. Miller, *J. Am. Chem. Soc.*, **71**, 1499 (1949).

(2) Available from the Lithium Corp. of America, Inc., Rand Tower, Minneapolis 2, Minn.

(3) This sample of lithium was kindly provided by the Lithium Corp. of America.

(4) K. Ziegler and H. Colonius, *Ann.*, **479**, 135 (1930); H. Gilman, E. A. Zoellner, and W. M. Selby, *J. Am. Chem. Soc.*, **54**, 1957 (1932); G. Wittig, *Angew. Chem.*, **53**, 241 (1940).

(5) Recently "sodium free" lithium was found to be unreactive toward *t*-butyl chloride. However, lithium containing 1–2% sodium gave good yields of *t*-butyllithium. See M. Stiles and R. P. Mayer, *J. Am. Chem. Soc.*, **81**, 1497 (1959).

sodium has to be intimately mixed with the lithium as the addition of pieces of sodium or sodium sand to the "low sodium" lithium does not change the yield. In the case of *n*-butyl bromide in diethyl ether the surface of the "low sodium" lithium coated badly which did not happen with regular lithium. The significance of this coating has not been evaluated. Further work is in progress on this effect of sodium on the preparation of *n*-butyllithium and other organolithium compounds. In this connection the yield of phenyllithium from bromobenzene and lithium seems to be unaffected by the amount of sodium in the lithium. It is considered likely that metals other than sodium may have an effect on the production of organolithium compounds and that this effect may apply to other organometallic compounds as well.

EXPERIMENTAL

Preparation of n-butyllithium in diethyl ether. The procedure outlined by Gilman *et al.*[1] using 1-bromobutane and lithium metal was followed. The resulting solution was filtered through glass wool, and the yield determined by the double titration method.[6] Any variations in procedure together with yields from specific runs are listed in Table I.

Preparation of n-butyllithium in benzene. As a basic procedure the lithium metal wire was cut into small pieces and washed several times with benzene to remove any grease. Then approximately 100 ml. of benzene was added before adding the 1-chlorobutane in benzene over a period of 0.5 hr. The temperature of the reaction was not controlled, and after the addition the reaction mixture was stirred for 3 hr. The double titration method[6,7] was used to determine the yield after filtering through glass wool. Any variations used in the procedure together with yields from specific runs are listed in Table II.

TABLE I

PREPARATION OF *n*-BUTYLLITHIUM FROM 1-BROMOBUTANE AND LITHIUM IN DIETHYL ETHER

Trial	Li, G.-Atoms	1-Bromobutane, Mole	Total Vol., Ml.	Temp.	Yield, %
1	0.67[a,b]	0.30	175	−35	37.0
2	0.34[a]	0.15	96	0	55.9
3	0.34[a]	0.15	135	−40	47.5
4	0.34[a]	0.15	105	−50	38.8
5	0.34[a]	0.15	94	10	58.8
6	0.34[a]	0.15	90	25	54.1
7	0.34[a]	0.075	100	0	57.7
8	0.34[a]	0.15[c]	135	−35	29.0
9	0.34[a,d]	0.15	112	−35	24.1
10	0.17[a] 0.20[e]	0.15	115	−35	76.0
11	0.36[f]	0.15	115	−35	72.5
12	0.41[g]	0.15	117	−35	76.8
13	0.34[a,h]	0.15	106	−35	53.4
14	0.40[a,i]	0.15	89	−35	53.4
15	0.40[a,i]	0.15	98	−35	41.5
16	0.40[a,j]	0.15	106	−35	49.8
17	0.40[a,j]	0.15	98	−35	45.0
18	0.40[a,h]	0.15	100	−35	47.0
19	0.40[k]	0.15	104	−35	84.2

[a] "Low sodium" lithium (0.002% Na). [b] Several small pieces of sodium added. [c] Addition time of halide was 3 hr. rather than the usual 30 min. [d] Lithium pressed to expose more surface. [e] Regular lithium (0.05% Na). [f] Sodium added to melted lithium. [g] Approximately 0.1% sodium added to melted lithium. [h] Small pieces of carefully handled sodium added. [i] Sodium bromide (0.1 g.) added. [j] Sodium sand (0.1 g.) added. [k] "High sodium" lithium (0.8% Na) from the Lithium Corp. of America, Inc.

TABLE II

PREPARATION OF *n*-BUTYLLITHIUM FROM 1-CHLOROBUTANE AND LITHIUM IN BENZENE

Trial	Li, G.-Atoms	1-Chlorobutane, Mole	Total Vol., Ml.	Temp.	Yield, %
1[a]	0.44[b]	0.19	147	—	32.3
2[a]	0.44[b]	0.19	125	—	57.5
3[a]	0.52[c]	0.19	250	—	37.0
4[e]	0.60[b]	0.19[d]	90	—	31.6
5[f]	0.60[b]	0.19[d]	173	—	39.5
6[g]	0.60[b]	0.19[d]	86	50–60	50.8
7[g]	0.60[h]	0.19[d]	109	—	77.2
8[i]	0.60[h]	0.19[j]	112	—	70.2

[a] Stirred 3 hr. at room temperature. [b] Regular lithium (<0.05% Na). [c] Lithium dispersion obtained from Lithium Corp. of America, Inc. [d] Entire amount of halide added at one time. [e] Mixture was shaken intermittently for 4 hr. [f] Stirred for 24 hr. with wire brush stirrer. [g] Stirred for 4 hr. with wire brush stirrer. [h] "High sodium" lithium (0.8% Na) from Lithium Corp. [i] Stirred with glass stirrer for 4 hr. [j] Halide was added during a period of 15 min.

Preparation of n-butyllithium in heptane. After washing the small pieces of lithium wire (0.56 g.-atom) several times in benzene, 35 ml. of heptane was added. Then a solution of 1-chlorobutane (0.15 mole) in 15 ml. of heptane was added rapidly (10 to 15 min.). When the addition was complete, the reaction mixture was stirred for 3 hr. After filtering through a sintered glass filter the yield was determined by the double titration method.[6,7] The yields are actually better than indicated because some of the *n*-butyllithium remained with the debris on the filter and could not be washed out with any reasonable amount of heptane. Any variations in

TABLE III

PREPARATION OF *n*-BUTYLLITHIUM FROM 1-CHLOROBUTANE AND LITHIUM IN HEPTANE

Trial	Li, G.-Atoms	1-Chlorobutane, Mole	Total Vol., Ml.	Temp.	Yield, %
1	0.56[a]	0.15[b]	54	65–75	52
2	0.56[a]	0.15[b]	66	65–75	52
3	0.56[a]	0.15[c]	58	65–75	61.8
4	0.56[d]	0.15[c]	66	65–75	67.6
5	0.65[d]	0.19[c]	65	65–75	69.9
6	0.56[e]	0.15[c]	62	65–75	65.1
7	0.65[e]	0.19[c]	61	65–75	65.7

[a] Regular lithium (<0.05% Na). [b] Addition time of halide was 15 min. [c] Addition time of halide was 10 min. [d] "High sodium" lithium (0.8% Na) from Lithium Corp. [e] "Low sodium" lithium (0.002% Na) from Lithium Corp.

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

(7) There seems to be some question about the accuracy of the double titration method in benzene and heptane solutions. However, the yields are consistent with each other though quite possibly low.

this procedure together with yields from specific runs are listed in Table III.

Acknowledgment. We wish to express our grateful appreciation to the Research Corp. for a grant which made this study possible.

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Oxidation of Nitrosoaromatic Compounds with Peroxytrifluoroacetic Acid[1]

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Received June 19, 1959

The previously unreported oxidation of *o*-dinitrosobenzene into *o*-dinitrobenzene has now been observed using peroxytrifluoroacetic acid.[2] Similar oxidations of 4-methyl-1,2-dinitrosobenzene into 4-methyl-1,2-dinitrobenzene and *p*-dinitrosobenzene into *p*-dinitrobenzene have occurred.

3-Nitro- and 3,5-dinitro-1,2-dinitrosobenzene, diphenylfuroxan, and the fused ring molecules, 1,2-dinitrosonaphthalene and 9,10-dinitrosophenanthrene apparently are not oxidized under similar conditions by peroxytrifluoroacetic acid into nitro derivatives and may be recovered. Poor recovery of the fused ring compounds indicates ring oxidation and degradation. Attempts to oxidize 4-chloro-5-methoxy-1,2-dinitrosobenzene with this reagent result in extensive destruction.

Peroxytrifluoroacetic acid oxidizes nitrosobenzene to nitrobenzene and catalyzes a self-condensation to *p*-nitrosodiphenylhydroxylamine.[3] Oxidation is predominant at higher temperatures and the condensation is predominant at lower temperatures.

$$C_6H_5NO \xrightarrow{F_3CCO_3H} C_6H_5NO_2 + p\text{-}ONC_6H_4N(C_6H_5)OH$$

EXPERIMENTAL

Oxidation of nitrosobenzene. To a solution of 3.21 g. (0.03 mol.) of nitrosobenzene in 25 ml. of methylene chloride, maintained at 5–10° with an ice bath, was added over a period of 45 min. with good stirring a solution of 1.2 ml. (0.04 mol.) of 90% hydrogen peroxide in 15 ml. (0.20 mol.) of trifluoroacetic acid. After the addition the solution was stirred another 15 min. at 5–10° and poured into 100 ml. of ice water. The mixture was made alkaline with solid sodium bicarbonate and allowed to stand for 4 hr. before the precipitated solid was collected, washed with 75 ml. of ether and air dried. The weight of crude yellow-brown *p-nitroso-N,N-diphenylhydroxylamine*, m.p. 138–141° dec. (lit.[3] m.p. 147–152° dec.), was 1.12 g. (35%). Recrystallization twice from aqueous ethanol (Norit) yielded 0.35 g. of yellow-brown solid, m.p. 137–138° (dec.).

A sample of the crude product dissolved in boiling aqueous ethanol was treated with zinc dust until the yellow color was discharged. After treating the mixture with Norit it was filtered and rapidly cooled. Grey platelets (which darkened in air) of *p*-aminodiphenylamine, m.p. 75–76° (lit.[4] m.p. 75°), separated from the solution. An attempt to carry out this reduction with sulfur dioxide as previously reported[3] allowed recovery of starting material.

The ether and methylene chloride layer of the filtrate from the oxidation reaction was separated and the aqueous phase was extracted with two 25-ml. portions of ether. The organic layer and the ether extracts were combined, washed with 25 ml. of water, and dried over anhydrous sodium sulfate. The solvent was removed, followed by distillation of a trace of a blue-green liquid (assumed to be nitrosobenzene), which was not isolated. Finally, 0.91 g. (25%) of nitrobenzene, b.p. 209–210°, n_{D}^{25} 1.5474, distilled as a dark yellow liquid. Redistillation gave a product b.p. 208–209°, n_{D}^{25} 1.5487, 0.63 g. (17%).

In another experiment nitrosobenzene was dissolved in 50 ml. of methylene chloride and, to the gently refluxing solution, a solution of hydrogen peroxide in trifluoroacetic acid was added over a period of 30 min. After refluxing another 15 min., the red-brown solution was poured into 150 ml. of ice water and worked up in the manner outlined above except that after filtering and washing the solid product with 25 ml. of cold methylene chloride, the combined filtrate and wash was steam distilled. The aqueous phase of the steam distillate was separated and extracted with two 15-ml. portions of methylene chloride. The combined extracts and methylene chloride layer of the distillate were dried over anhydrous sodium sulfate. By distillation of this solution there was obtained 1.31 g. (35.5%) of nitrobenzene, b.p. 208–210°, n_{D}^{25} 1.5484. The crude dry *p*-nitroso-*N*,*N*-diphenylhydroxylamine filtered from the reaction mixture weighed 0.49 g. (15%), m.p. 120° (dec.). Recrystallization from aqueous ethanol furnished 0.25 g. (8%) of material, m.p. 128–132° (dec.).

Oxidation of 1,2-dinitrosobenzene. To a solution of 2.70 g. (0.12 mol.) of the dinitroso compound in 15 ml. (0.20 mol.) of trifluoroacetic acid was added with stirring 1.7 ml. (0.06 mol.) of 90% hydrogen peroxide. The solution was heated to reflux and the heat of reaction was sufficient to maintain reflux for a few minutes. After a total reflux time of 45 min. the solution was poured into 200 ml. of ice water, the crude yellow precipitate of *o*-dinitrobenzene was filtered, washed with water, and recrystallized from dilute ethanol as light yellow needles, m.p. and mixture m.p. 118–119° (lit.[5] m.p. 116–116.5°), 0.71 g. (21%). Comparable yields of *o*-dinitrobenzene were obtained when the reaction was carried out in the presence of urea, a scavenger for oxides of nitrogen, either at room temperature for 17 hr. or at reflux for 1 hr.

In a similar manner, 3,4-dinitrosotoluene was oxidized into dinitrotoluene, m.p. and mixture m.p. 58–59°,[6] in 15% yield and *p*-dinitrosobenzene into *p*-dinitrobenzene, m.p. and mixture m.p. 174–175°,[5] in 92% yield.

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[1] Financial support by the Office of Ordnance Research, U. S. Army under contracts No. DA-01-009-ORD-428 and DA-01-009-ORD-669.

[2] A. S. Bailey and J. R. Case, *Tetrahedron*, **3**, 113 (1958) report that performic and peracetic acids do not react with *o*-dinitrosobenzene.

[3] E. Bamberger, H. Büsdorf, and H. Sand, *Ber.*, **31**, 1513 (1898).

[4] O. Fischer and L. Wacker, *Ber.*, **21**, 2609 (1888).

[5] J. W. Williams and C. H. Schwingel, *J. Am. Chem. Soc.*, **50**, 362 (1928).

[6] F. Beilstein and A. Kuhlberg, *Ann.*, **155**, 1 (1870).