treatment of the saponification mixture with semicarbazide reagent.

6-Phenyl-5-hydroxy-5-hexenoic acid δ-lactone (*Lactone 1, Table II*) *from* (I) (*R = phenyl, n = 2*). Commercial peroxyacetic acid[20] (12 ml. containing 0.076 mole peracid) was added with stirring during 10 min. to benzalcyclopentanone (14.05 g., 0.082 mole) in glacial acetic acid saturated with potassium acetate (70 ml.). After 40 min., about 93% of the peroxyacetic acid and 53% of the hydrogen peroxide content of the reagent had been consumed; after 70 min. about 95% and 68%, respectively, had been consumed. Ether and water (100 ml. each) were added to the reaction mixture. The aqueous layer was separated and extracted twice with ether (50 ml.). The ethereal solutions were combined, washed consecutively with water (3 × 50 ml.), sodium carbonate solution (2 × 25 ml.), and again with water (2 × 50 ml.). After filtration through magnesium sulfate and concentration on the steam bath, a residue was obtained which solidified on cooling. By recrystallization from isopropyl ether it yielded colorless flakes, m.p. 79–80° (8.4 g.).

Anal. Calcd. for $C_{12}H_{12}O_2$: C, 76.58; H, 6.43. Found: C, 76.39; H, 6.29.

Somewhat less pure additional material (1.0 g.) was isolated from the recrystallization mother liquors. Total yield obtained: 67% on the basis of peroxyacetic acid, 62% on the basis of the ketone used.

Potassium permanganate oxidation of 7-phenyl-6-hydroxy-6-heptenoic acid ε-lactone (VII). The lactone (2.02 g., 0.01 mole) was oxidized by stirring it with 2% potassium permanganage solution (450 ml.) for 16 hr. at room temperature. Potassium carbonate (5.0 g.) was added and stirring continued for 2 hr. Several small portions of oxalic acid were added to the mixture with warming on the steam bath, until the purple color of the solution was discharged. The resulting mixture was filtered and the filtrate evaporated on the steam bath. The solution of the residue in water (50 ml.) was acidified to *p*H 5. Solid benzoic acid separated and was removed by filtration. The filtrate was extracted twice with ether (15.10 ml.). On concentration, the ethereal extracts yielded adipic acid. Both acids were identified by their neutralization equivalents and melting points, taken separately and admixed with authentic specimen.

Peroxyacetic acid oxidation of lactones (III). A solution of 6-phenyl-5-hydroxy-5-hexenoic acid δ-lactone (Lactone I, Table II) in acetic acid saturated with potassium acetate (12 ml. solution containing 1.30 g., 5.9 millimoles, of lactone) was treated with peroxyacetic acid (2 ml. containing 6.8 millimoles of peracid and less than 0.24 millimole of hydrogen peroxide). After 1 hr., the peroxyacetic acid had been consumed. The reaction mixture was poured into water (30 ml.) and the precipitated oil was allowed to crystallize. The crystallized material was separated by filtration, washed with water and low boiling petroleum ether; after recrystallization from isopropyl ether it had m.p. 80° (0.73 g., 52% yield). Additional material was obtained by working up the recrystallization mother liquors.

Anal. Calcd. for $C_{12}H_{12}O_3$: C, 70.57; H, 5.93; Sapon. equiv. 204. Found: C, 70.72; H, 5.99; Sapon. equiv. 207.

Saponification of lactone (V). The above lactone (0.10 g.) was saponified in 0.2*N* potassium hydroxide in 50% alcohol (3 ml.) at room temperature. The saponification mixture was acidified with hydrochloric acid; the precipitated organic acid was filtered and washed with water, after air-drying, the acid was recrystallized from a mixture of carbon tetrachloride and petroleum ether and then from carbon tetrachloride; it had m.p. 62° and neut. equiv. 221 (calcd., 222).

Acknowledgment. The author is indebted to S. J. Tassinari for the microanalyses reported.

OAKDALE, N. Y.

---

[20] "Becco 40% Peracetic Acid" was obtained from the Becco Chemical Division, Food Machinery and Chemical Corp., Buffalo 7, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Preparation and Stability of Some Organolithium Compounds in Tetrahydrofuran

HENRY GILMAN AND BERNARD J. GAJ

Received April 15, 1957

Methyl-, *n*-butyl-, and phenyllithium have been prepared in tetrahydrofuran by the interaction of methyl chloride, *n*-butyl chloride, *n*-butyl bromide, and bromobenzene, respectively, with lithium wire. The stability of these reagents in tetrahydrofuran at several temperatures has been studied. The order of stability was found to be: methyl- > phenyl- > *n*-butyllithium.

A number of studies concerned with the cleavage of ethers by organometallic reagents have been reported;[1] however, only three of these studies[1i, 1s, 1t] involved reactions of tetrahydrofuran

---

[1] (a) K. Ziegler and A. Colonius, *Ann.*, **479**, 135 (1930); (b) J. W. Cook, C. L. Hewett, and C. A. Lawrence, *J. Chem. Soc.*, **1936**, 71; (c) W. Huckel and H. Bretschneider, *J. prakt. Chem.*, **151**, 61 (1938); (d) A. Lüttringhaus and G. Wagner-v. Sääf, *Angew. Chem.*, **51**, 915 (1938); (e) A. H. Haubein, *Iowa State Coll. J. Sci.*, **18**, 48 (1943) [*Chem. Abstr.*, **38**, 716 (1944)]; (f) A. A. Morton, *Chem. Revs.*, **35**, 21 (1944); (g) A. Lüttringhaus, G. Wagner-v. Sääf, E. Sucker, and G. Borth, *Ann.*, **557**, 46 (1947); (h) B. C. McKusick, *J. Am. Chem. Soc.*, **70**, 1976 (1948); (i) G. Wittig and A. Rückert, *Ann.*, **566**, 101 (1950); (j) K. Ziegler and H. G. Gellert, *Ann.*, **567**, 185 (1950); (k) S. J. Cristol, J. R. Douglass, and J. S. Meek, *J. Am. Chem. Soc.*, **73**, 816 (1951); (l) D. H. Gould, K. H. Schaaf, and W. L. Ruigh, *J. Am. Chem. Soc.*, **73**, 1263 (1951); (m) R. L. Letsinger, A. W. Schnizer, and E. Bobko, *J. Am. Chem. Soc.*, **73**, 5708 (1951); (n) R. L. Letsinger, J. H. Traynham, and E. Bobko, *J. Am. Chem. Soc.*, **74**, 399 (1952); (o) P. D. Bartlett, S. Friedman, and M. Stiles, *J. Am. Chem. Soc.*, **75**, 1771 (1953); (p) R. L. Letsinger and E. Bobko, *J. Am. Chem. Soc.*, **75**, 2649 (1953); (q) A. A. Morton and E. Brachman, *J. Am. Chem. Soc.*, **76**, 2973 (1954); (r) H. Gilman, A. H. Haubein, and H. Hartzfeld, *J. Org. Chem.*, **19**, 1034 (1954); (s) H. Normant, *Compt. rend.*, **239**, 1510 (1954); (t) R. L. Letsinger and D. F. Pollart, *J. Am. Chem. Soc.*, **78**, 6079 (1956).

with organometallic reagents. Wittig and Rückert[1i] reported that tetrahydrofuran, when complexed with triphenylboron, could be cleaved by triphenylmethylsodium. Letsinger and Pollart[1t] reported that tetrahydrofuran was fairly stable toward cleavage by propylsodium at 50°, and Normant[1s] reported that the tetrahydrofuran-Grignard complex can be cleaved at temperatures above 200°.

Recently tetrahydrofuran has been used as a solvent for a number of reactions involving organolithium reagents.[2] These reactions either do not proceed in diethyl ether or they proceed at a much slower rate and in appreciably lower yields. Among these reactions are the preparation of some dihalobiphenyls from dihalobenzenes and *n*-butyllithium[2a] (prepared in diethyl ether); the preparation of aryllithium compounds from aryl chlorides and fluorides;[2b, 2c] the cleavage of a number of heterocyclic compounds by lithium;[2d] and the metalation of dibenzofuran and aryl fluorides with *n*-butyllithium.[2e, 2f] The pronounced effect of tetrahydrofuran in facilitating metalation reactions and displacement reactions in a mixed solvent system (tetrahydrofuran—diethyl ether), and the desire to investigate some of these reactions in tetrahydrofuran alone, led to the present study involving the preparation and chemical stability of methyl-, *n*-butyl-, and phenyllithium in tetrahydrofuran.

Phenyllithium can be prepared from bromobenzene and lithium wire in tetrahydrofuran at −60° in yields up to 98%. The preparation of organolithium compounds in diethyl ether at such low temperatures has not been reported. Higher reaction temperatures consistently resulted in lower yields of phenyllithium in tetrahydrofuran. In contrast to the preparation of *n*-butyllithium in diethyl ether, this same organolithium compound could be prepared in higher yields from *n*-butyl chloride than from *n*-butyl bromide in tetrahydrofuran. Methyllithium could not be prepared in tetrahydrofuran from methyl iodide and lithium at temperatures ranging from 0° to −30°, but it could be prepared in yields up to 77% from liquified methyl chloride at −10°.

The decreased yields of phenyllithium at temperatures above −60°, the lower yields of *n*-butyllithium obtained from the bromide as compared to the chloride and the inability to prepare methyllithium from the iodide in tetrahydrofuran can be rationalized on the basis of previous results. The coupling reaction, a nucleophilic displacement of a halide in the organic halide by the anion of the organolithium compound, appears to be enhanced in tetrahydrofuran, *e.g.*, dihalobiphenyls are readily formed at low temperatures by the interaction of *n*-butyllithium with dihalobenzenes;[2a] also certain Grignard reagents and organolithium compounds couple smoothly with chlorosilanes at low temperatures.[3] The marked effect of tetrahydrofuran on facilitating displacement reactions, together with the decreasing ease of displacement in a bimolecular, nucleophilic substitution reaction for the series I, Br, and Cl, can be correlated with the dependence of the organolithium yields on the particular alkyl or aryl halide employed. Although methyllithium could not be prepared from methyl iodide in tetrahydrofuran, presumably because of coupling, the organolithium compound can be prepared in 64–70% yields from liquified methyl chloride and lithium in the same solvent. When gaseous methyl chloride was bubbled through a mixture of lithium and tetrahydrofuran until all of the lithium was consumed, the yield of methyllithium dropped to 23%. It is not necessary for lithium to participate in the coupling reaction because it has been observed that methyllithium, prepared in tetrahydrofuran at −10° in the presence of an excess of methyl chloride, upon warming to 0°, gives a negative Color Test I.[4] Methyllithium in the absence of an excess of organic halide is quite stable at room temperature (see Table III).

Methyl-, *n*-butyl-, and phenyllithium have been found to be less stable in tetrahydrofuran than in diethyl ether.[1e,1r] As expected, the order of stability of the three organolithium reagents investigated was the same as the order found in diethyl ether,[1e,1r] namely, methyl- > phenyl- > *n*-butyllithium. Examination of the stability data (Tables I and III), indicates that workable temperatures for methyl-, *n*-butyl-, and phenyllithium in tetrahydrofuran are 0°, below −35°, and 0 to −30°, respectively.

It is interesting to note that the sensitivity of Color Test II[5] appears to be much lower in tetrahydrofuran than in diethyl ether. When the concentration of *n*-butyllithium, as determined by the double titration procedure,[6] had decreased to about 0.2*M*, the solution no longer gave a positive Color Test II in tetrahydrofuran; however, Color

---

(2) (a) H. Gilman and B. J. Gaj, *J. Org. Chem.*, **22**, 447 (1957); (b) H. Gilman and T. Soddy, *J. Org. Chem.*, **22**, 565 (1957), (c) H. Gilman and T. Soddy, *J. Org. Chem.*, **22**, 1121 (1957); (d) H. Gilman and J. J. Dietrich, *J. Org. Chem.*, **22**, 851 (1957); (e) H. Gilman and R. D. Gorsich, *J. Org. Chem.*, **22**, 867 (1957); (f) H. Gilman and T. Soddy, *J. Org. Chem.*, in press. See, also, H. Gilman and R. D. Gorsich, *J. Am. Chem. Soc.*, **77**, 3134 (1955); G. Wittig and L. Pohmer, *Chem. Ber.*, **89**, 1334 (1956); H. Heaney, F. G. Mann, and I. T. Millar, *J. Chem. Soc.*, 4692 (1956).

(3) (a) Allylmagnesium chloride has been found to couple instantaneously at −35° with triphenylchlorosilane in tetrahydrofuran (unpublished studies of B. J. Gaj); (b) triphenylsilyllithium couples readily with triphenylchlorosilane below −60° in good yield in tetrahydrofuran (unpublished studies of G. D. Lichtenwalter); (c) in this study, methyllithium coupled smoothly with triphenylchlorosilane at −35° in tetrahydrofuran.

(4) H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

(5) H. Gilman and J. Swiss, *J. Am. Chem. Soc.*, **62**, 1847 (1940).

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

TABLE I

STABILITY OF METHYLLITHIUM IN TETRAHYDROFURAN

Size Aliquot	Hr. at t, °C.	t, °C.	Triphenylmethylsilane,[a] Wt.	Yield,[b] %
25	0	−10	4.78	71.1
50	1	0–3	8.95	66.6
50	1	0–3	8.40	62.5
50	2.5	0–3	8.00	59.5
—	2	0–3	—	—
50	2	25	5.87	43.7
50	12	25	4.97	37.0
80	13	65	2.97	13.8

[a] These fractions all melted within the range 65–68°. [b] The yields are based on the titration yield taken as 100%.

TABLE II

PREPARATION OF RLi COMPOUNDS IN TETRAHYDROFURAN[a]

RX	RX, Mole	Lithium, g.-atoms	t, °C	Yield,[b,c] %
Bromobenzene	0.3	1.5	−35	77
Bromobenzene	0.3	1.5	−40	81
Bromobenzene	0.3	1.5	−50	82
Bromobenzene	0.6	1.5	−60	92
n-Butyl chloride	0.25	1.0	−30	75
n-Butyl chloride	0.5	1.25	−25	77
n-Butyl bromide	0.2	1.0	−60	56
Methyl chloride	0.37	0.89	−10	70

[a] Reactions described in the experimental part have been excluded from this table. [b] The yields of phenyllithium and methyllithium were determined by acid titration. [c] The yields of *n*-butyllithium were determined by the double titration method.

TABLE III

STABILITY OF PHENYL- AND *n*-BUTYLLITHIUM IN TETRAHYDROFURAN[a]

RLi	Time at t°C., Hr.	t, °C.	Molarity	Yield,[b,c] %	Color Test I	Color Test II
1. Phenyllithium	0	−20	0.77	100	+	
	7[d]	65	—	1.0	+	
2. Phenyllithium	0	0	0.88	100	+	
	10	25	—	67	+	
	2	65	—	18	+	
3. *n*-Butyllithium	0	−30	0.99	100	+	+
	12	−30	0.94	95	+	+
	10	10	0.20	20	+	−
	2	27	0.00	0.00	−	−
4. *n*-Butyllithium	0	0	1.04	100	+	+
	22.5	0	0.62	60	+	+
	15	0	0.20	19	+	−
	9.5	0	0.00	0.00	−	−

[a] Reactions described in the experimental part have been excluded from this table. [b] The yields are based on the titration yield taken as 100%. [c] The decrease in yield of phenyllithium was followed by carbonation of aliquots, while for *n*-butyllithium the double titration procedure was used. [d] In another run, Color Test I became negative after refluxing for 11 hr.

Test I persisted until all of the *n*-butyllithium had been utilized, as indicated by a double titration of an aliquot. The minimum concentration of *n*-butyllithium necessary to give a positive Color Test II is $0.03M$ in diethyl ether.[5] This suggests that Color Test II, if used at all to detect alkyllithium reagents in tetrahydrofuran, should be used with discretion.

EXPERIMENTAL[7]

Phenyllithium, Run I. A solution of 94.2 g. (0.6 mole) of bromobenzene in 400 ml. of anhydrous tetrahydrofuran[8] was added over a 3-hr. period to a suspension of 10.4 g. (1.5 g.-atoms) of finely cut lithium wire in 200 ml. of tetrahydrofuran. The reaction was initiated and maintained at a temperature of −60 ± 5° during the entire addition by means of a Dry Ice-acetone bath. A pale pink color developed after the first 5 ml. of the bromobenzene solution was added. The color progressively darkened to deep red at the end of the addition. Upon completion of the addition, the reaction mixture was stirred at −50° for 1 hr., then stirred overnight while being cooled by a Dry Ice-acetone bath. The temperature was allowed to rise to 0° and the unreacted lithium was removed by filtration through a plug of glass wool into a calibrated addition funnel. The yield, as determined by acid titration,[9] was 655 ml. of $0.8M$ phenyllithium (87.5%).

The red solution was stirred at room temperature for 24 hr. A 100-ml. aliquot was removed and carbonated by pouring jet-wise onto a Dry Ice-ether slurry. The carbonation mixture was worked up in the usual manner to give 4.74 g. (48%) of crude benzoic acid, m.p. 114–123°. Sublimation of this material under reduced pressure gave 3.73 g. (38%) of pure benzoic acid, melting point and mixed melting point with an authentic sample, 122–123°, and 0.15 g. (1.8%) of less pure acid, m.p. 118–122°. No attempt was made to purify the dark-brown, sublimation residue.

The remaining phenyllithium solution was refluxed for 1.5 hr. and a 200-ml. aliquot was carbonated. Work-up in the usual manner yielded 6.57 g. of a brown, sticky material which appeared to melt over the range 107–124° to a dark-brown liquid. Sublimation of this material yielded 2.31 g. (12%) of benzoic acid, melting point and mixed melting point with an authentic sample, 122–123°, and a non-sublimable, dark, amorphous residue which was not purified or identified. The remaining 355 ml. of phenyllithium was carbonated after refluxing an additional 1.5 hr. Sublimation of the dark-brown, tarry material obtained by work-up in the usual manner, gave about 1 g. (3%) of benzoic acid, m.p. 120–123° and 8 g. of an amorphous, dark solid similar to that obtained from the previous aliquots.

Run II. In order to determine how close the titration yield agreed with the yield upon carbonation, this reaction was repeated on a smaller scale and the mixture was carbonated after filtration and titration. The quantities of materials used were 3.5 g. (0.5 g.-atom) of lithium in 25 ml. of tetrahydrofuran and 15.7 g. (0.1 mole) of bromobenzene in 75 ml. of tetrahydrofuran. The addition was made over a 2-hr. period at −60 ± 5°. The reaction mixture was stirred at this temperature for 3 hr. after the addition, at which time it was noticed to be green. Upon warming the mixture to −35°, the lithium began to clump together and the red

---

(7) All reactions were carried out under an atmosphere of dry, oxygen-free nitrogen, and all melting points are uncorrected. The Color Test II referred to in these experiments is the one involving *p*-bromo-*N*,*N*-dimethylaniline.

(8) The tetrahydrofuran used in these experiments was dried and purified by preliminary refluxing over sodium wire for at least 24 hr. followed by distillation into a receiver containing lithium aluminum hydride from which it was distilled immediately before use.

(9) H. Gilman, P. D. Wilkinson, W. P. Fishel, and C. H. Meyers, *J. Am. Chem. Soc.*, **45**, 150 (1923).

color returned. The solution was cooled to the minimum temperature afforded by a Dry-Ice-acetone bath and held at this temperature overnight. The mixture was warmed to −35°, filtered and a 2-ml. aliquot was titrated.[9] The yield was 97%. Carbonation of the red solution, followed by work-up in the usual manner, yielded 11.9 g. (97.5%) of crude acid, m.p. 118–120°. Recrystallization from an ethanol-water pair gave 5.5 g. of benzoic acid, m.p. 122–123° and 5.6 g. of less pure acid, m.p. 121–123° (91%).

Several additional preparations of phenyllithium were made in tetrahydrofuran, the essentials of which are given in Tables II and III.

n-Butyllithium. (*a*). *From n-butyl chloride.* A solution of 64.8 g. (0.7 mole) of *n*-butyl chloride in 300 ml. of tetrahydrofuran was added over a 1.66-hr. period to a stirred suspension of 13.94 g. (2 g.-atoms) of finely cut lithium wire in 300 ml. of tetrahydrofuran. The reaction mixture was maintained at −25 ± 5° during the addition and for 1 hr. thereafter by means of a Dry Ice-acetone bath. The excess lithium was removed by filtration in the manner described for phenyllithium. The yield, as determined by the double titration method,[6] was 658 ml. of 0.79*M* *n*-butyllithium (74%). The solution was warmed to room temperature[10] during a 10-min. period. An aliquot was titrated by the double titration procedure[6] after stirring for 1 hr. at room temperature. The molarity of the solution had decreased to 0.23. Color Test II[5] was found to be negative 15 min. later, at which time the molarity was 0.20. After stirring at room temperature for an additional 3.75 hr., Color Test I became negative, and titration of an aliquot indicated that all of the *n*-butyllithium had been consumed.

The results of several additional preparations of *n*-butyllithium from *n*-butyl chloride are given in Tables II and III.

(*b*). *From n-butyl bromide. Run I.* *n*-Butyllithium was prepared from 3.5 g. (0.5 g.-atom) of lithium in 70 ml. of tetrahydrofuran and 27.4 g. (0.2 mole) of *n*-butyl bromide in 130 ml. of tetrahydrofuran. The addition was made at −60 ± 5° over a 2-hr. period. The mixture was stirred for 1 hr. at the same temperature before it was filtered and titrated. The yield was 56% by double titration.

Run II. The reaction was repeated under the same conditions except that 6.94 g. (1.0 g.-atom) of lithium metal was used. There was no increase in yield.

Methyllithium. (*a*). *From liquified methyl chloride.* The apparatus used for this preparation consisted of a 500-ml., four-necked flask which was fitted with a Dry Ice-acetone condenser, low-temperature thermometer, Truebore stirrer, and a jacketed, addition funnel containing a Dry Ice-acetone mixture in the outer jacket.

A suspension of 9.3 g. (1.33 g.-atoms) of lithium wire in 300 ml. of tetrahydrofuran was introduced into the flask and cooled to −10 ± 2° by means of a Dry Ice-acetone mixture. A solution of 27.6 g. (0.545 mole) of liquid[11] methyl chloride in 50 ml. of tetrahydrofuran, cooled with a Dry Ice-acetone bath, was added over a 45-min. period. After completion of the addition the gray suspension was stirred at −10 ± 2° for 30 min. The mixture was cooled to −35°, filtered to remove unreacted lithium and rewarmed to −10°. Acid titration[9] indicated a yield of 355 ml. of 0.986*M* methyllithium (64%). The solution was transferred, while still at −10°, to a three-necked flask which had been cooled previously to −10°. Aliquots were removed at various times and temperatures, and these were derivatized at −35° with triphenylchlorosilane. Each derivatized aliquot was hydrolyzed with saturated ammonium chloride. The organic layer was evaporated to remove tetrahydrofuran and the residue was dissolved in a 1:1 mixture of benzene and petroleum ether (b.p. 60–70°). The resulting solution was chromatographed through an alumina column. The eluant was passed through until evaporation of a 2-ml. portion of the eluate indicated the absence of triphenylmethylsilane. The eluate was evaporated and the yield of triphenylmethylsilane determined. After recrystallization from petroleum ether (b.p. 28-38°), the product was identified by a mixed melting point with an authentic sample. The melting point and mixed melting point of the recrystallized product with an authentic sample, was 67–68°, lit.[12,13] 67°. The results of this experiment are given in Table I.

(*b*). *From gaseous methyl chloride.* Methyllithium was prepared in 23% yield when gaseous methyl chloride was bubbled through a suspension of 0.56 g. (0.08 g.-atom) of lithium wire in 50 ml. of tetrahydrofuran at −10°. The methyl chloride was bubbled through the mixture until all of the lithium was consumed, and the yield was determined by isolating triphenylmethylsilane from the reaction of the methyllithium with an excess of triphenylchlorosilane. The yield was 2.48 g. (23%) of triphenylmethylsilane, m.p. 67–68°.

In a similar reaction, gaseous methyl chloride was bubbled through a mixture of lithium and tetrahydrofuran at −10° for 5 min. after all of the lithium had been consumed. A single acid titration of an aliquot indicated a yield of 12%. Color Test I became negative upon warming to 0° indicating the absence of any organolithium compound.

Attempted preparation of methyllithium from methyl iodide. Several attempts were made to prepare methyllithium from methyl iodide and lithium in tetrahydrofuran at 0° to −30°. A reaction did occur, as was evidenced by the bright surface on the metal, gas evolution at 0° to −10°, and the formation of a gray suspension in the reaction mixture. However, Color Test I was negative throughout the reaction.

Acknowledgment. This work was supported in part by the United States Atomic Energy Commission under Contract No. AT(11-1)-59, incidental to a study concerned with organic liquid solution scintillators.

AMES, IOWA

---

(10) Cooling was required to hold the temperature at 25°, since the reaction became exothermic as soon as room temperature was reached.

(11) The gaseous methyl chloride was liquified by passing the compressed, dry gas through a 50-ml., long-necked, glass-stoppered flask, whose bulb was immersed in a Dry Ice-acetone bath. The cold flask was weighed before and after transfer to the addition funnel.

(12) C. A. Kraus and H. Eatough, *J. Am. Chem. Soc.*, **55**, 5008 (1933).

(13) H. Marsden and F. S. Kipping, *J. Chem. Soc.*, **93**, 198 (1908).